DOE Carbon-based Materials Center of Excellence: Overview and NREL Activities

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This presentation contains no proprietary information

ST 18 & STP 30

Overview: Timeline and Budget

Timeline

- Work at NREL since FY93
- Center of Excellence start date: FY05
- Center of Excellence end date: FY09
- Percent complete: 10%

Budget

- Project funding
  - $27.5 M for five-year Center of Excellence
  - $2.5 M Contractor share (20% of Contractor budget)
  - $2 M in FY04 for NREL
  - $2 M in FY05 for NREL

Overview: Barriers & Targets

General

A. Cost.
B. Weight and Volume.
C. Efficiency.
E. Refueling Time

Reversible Solid-State Material

M. Hydrogen Capacity and Reversibility.
N. Lack of Understanding of H Physi- and Chemisorption.
O. Test Protocols and Evaluation Facilities.

Crosscutting Relevance

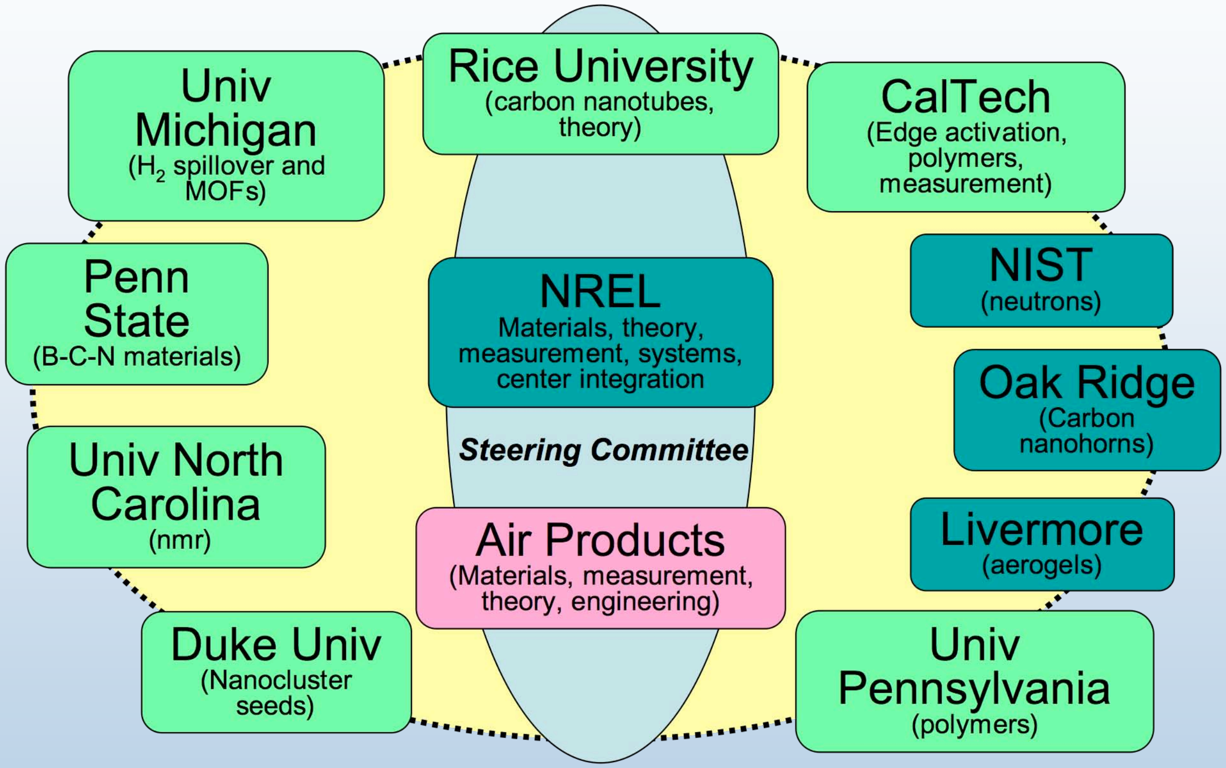
Compressed Gas Systems Barrier H: Sufficient Fuel Storage for Acceptable Vehicle Range.
Off-Board Hydrogen Storage Barriers S & T: Cost and Efficiency

DOE 2010 Technical Targets for Storage System

- Gravimetric 0.06 kg H_2/ kg
- Volumetric 0.045 kg H_2/ kg

Overview:
CoE Interactions & Collaborations

9 university projects (at 7 universities), 4 government labs, 1 industrial partner



Also: *IEA Annex 17 (R. Chahine, K. Ross), SwRI, Stanford GCEP, U. Minn. IREE, NIST, NASA, Virginia Commonwealth U. (G. Glaspell), Chinese Academy of Sciences (H.-M. Cheng), Argonne National Lab (R. Ahluwalia), synergy with two BES projects at NREL*

Organization of Conferences: *IPHE (Lucca, 6/'05), MRS (Fall '04, Fall '05, and Spring '05)*

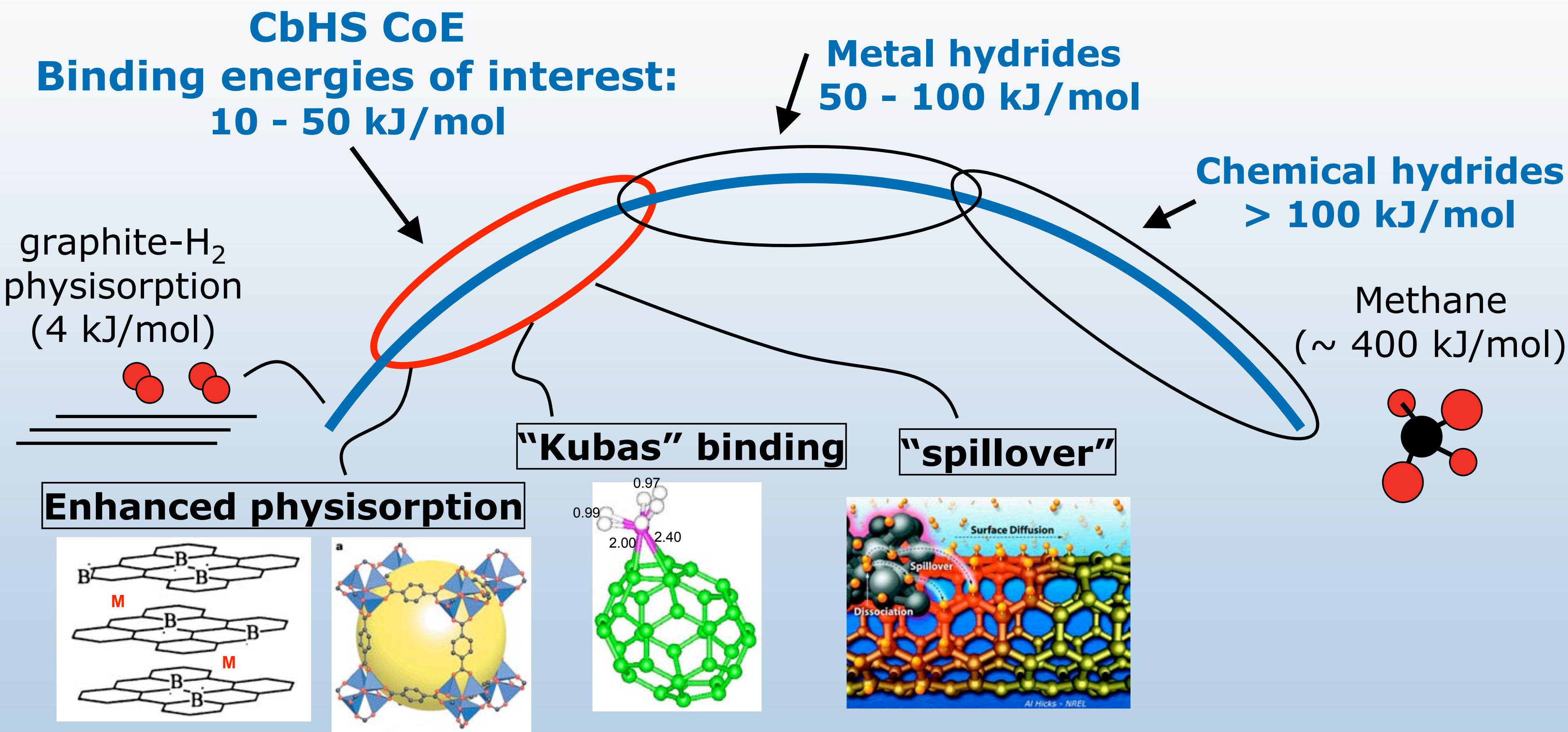
Objectives

Themes of CbHS Center of Excellence

- Develop conducting and boron/carbon polymers, MOFs, carbon nanohorns, nanotubes and aerogels, and carbon-metal nanomaterials for on-vehicle storage
- Design and synthesize materials that bind hydrogen as either (i) weakly and reversibly bound atoms or (ii) as strongly bound molecules.
- Synthesize, test, develop light materials with high densities of appropriate binding sites per volume to meet DOE goals
- New concepts (e.g. conformal tanks with low T moderate P (<100 bar) operation, nanotube/hydride mixtures)

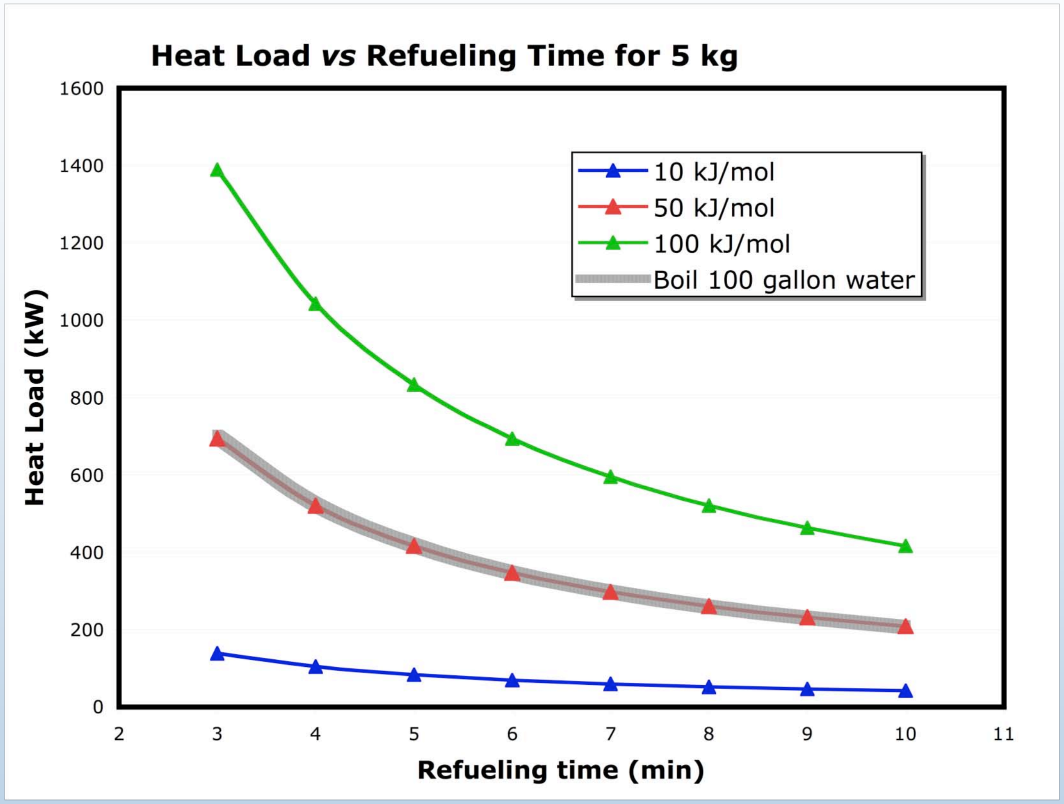
Continuum of H Binding Energies

and three Centers of Excellence



CbHS CoE: Nanostructural design of electronic & bond strain effects

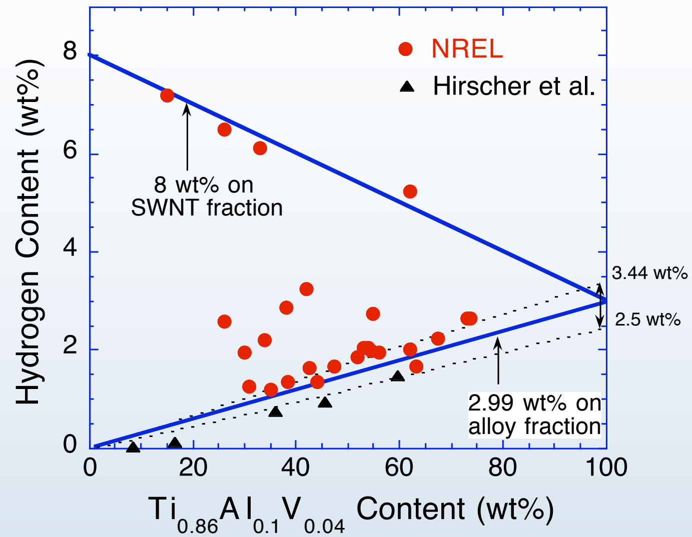
Binding Energy Impacts System Design



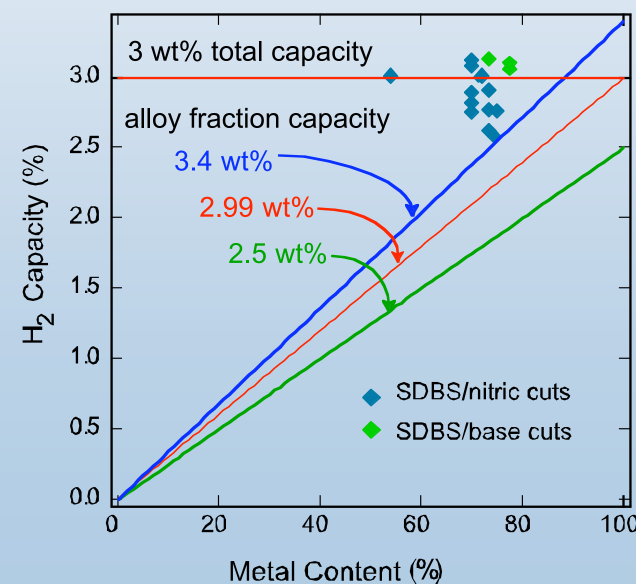
A large binding energy will lead to energy penalties during charge & discharge, prohibit on-board recharging, and reduce system capacities (heat exchangers)

Approach: Reproducible Activation

- Probe-sonicated SWNT/alloy hybrid data was scattered
- Up to 8 wt% H on tube fraction
- Contribution of alloy measured to be 2.5 wt% H
- Maximum on alloy 2.99 wt% (literature) or 3.4 wt% (TiH_2 fraction @ 4 wt%)



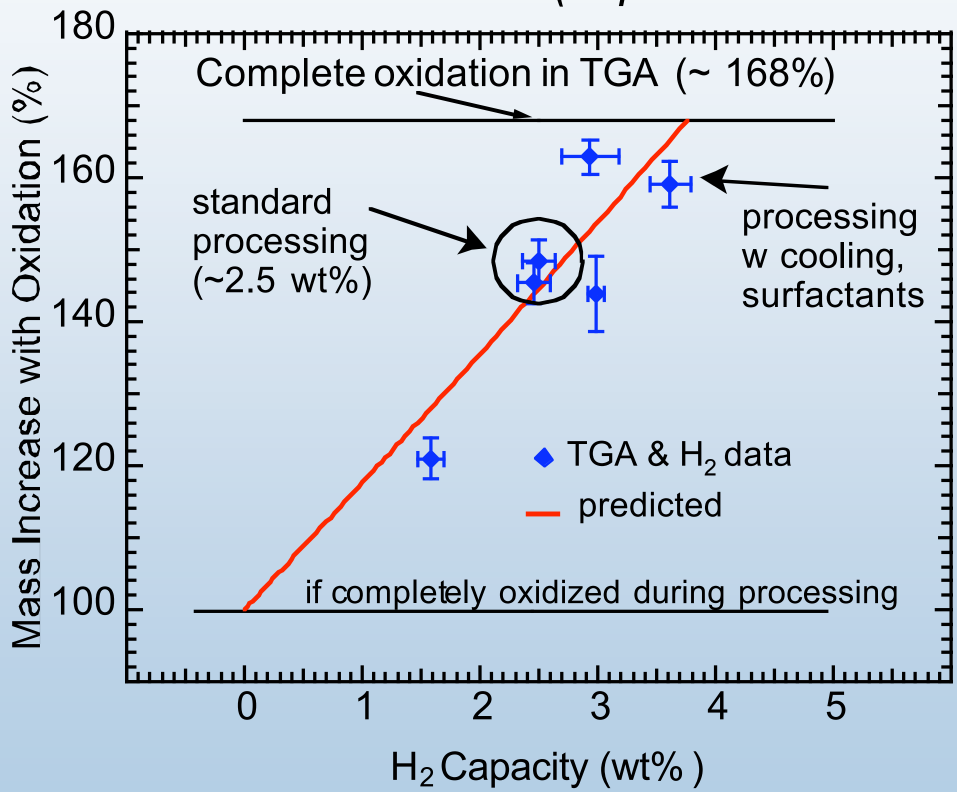
- Generated 3 wt% samples consistently with optimization
- Employed surfactants and cooling during sonication
- XRD reveals lack of alloy oxides
- Unoxidized alloy fraction adsorbs ~3.8 wt% H (Feb. 05 milestone)
- No significant uptake on tubes



Accomplishment: Measured Uptake of Alloy/Alloy Oxide *vs* Processing

- *Oxide coating on alloy particles is a function of processing*
- *3.8 wt% on pure alloy measured for the first time*

(importance to nuclear industry)

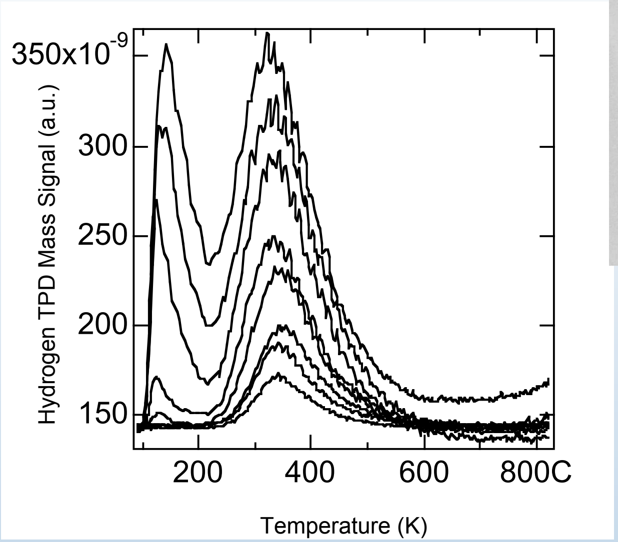


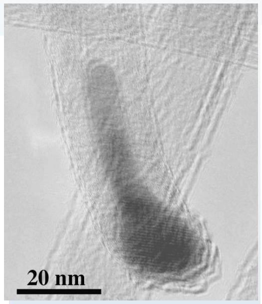
4 wt% H milestone will likely not be met with this approach (EOFY05)

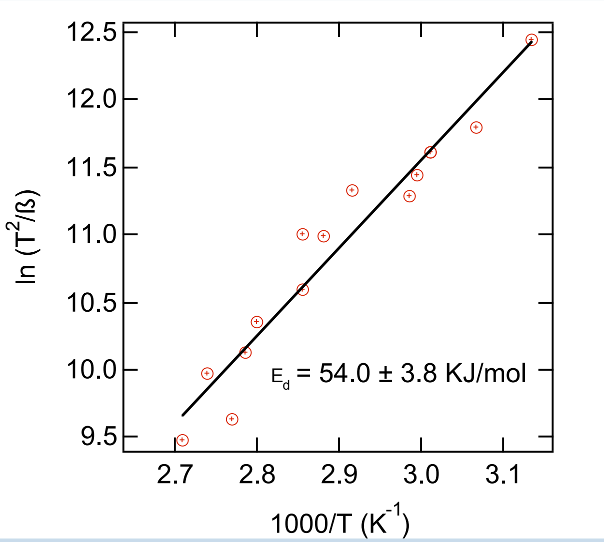
Approach: Reproducible Activation

MWNTs by hot-wire CVD (A. Dillon et al.)

- Fe is in intimate contact with aromatic carbon







Peak desorption temperature does not shift with coverage:

- first order desorption - adsorbed molecular H_2

Desorption activation energy:

$\ln(T_m{}^2/\beta) = E_d/RT_m$

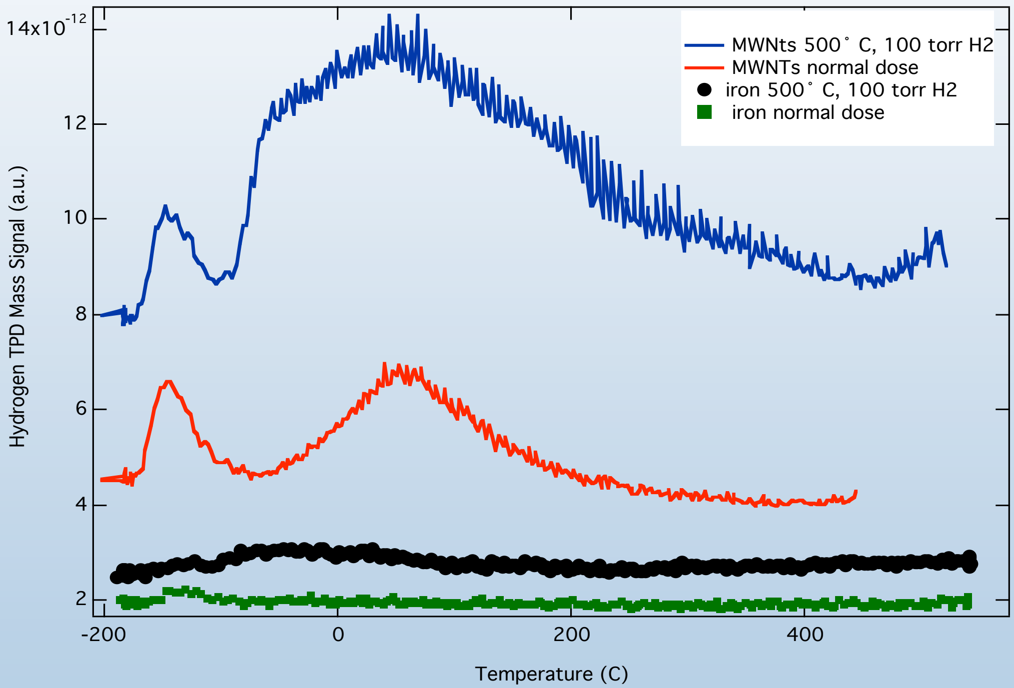
- binding energy of ~54 kJ/mol.

Microscopy by Y.-W. Lee, B.M. Clemens (Stanford)

Activation without Metal-Hydride Incorporation

As-synthesized MWNTs *vs* Fe powder control

Fe is not a known metal hydride

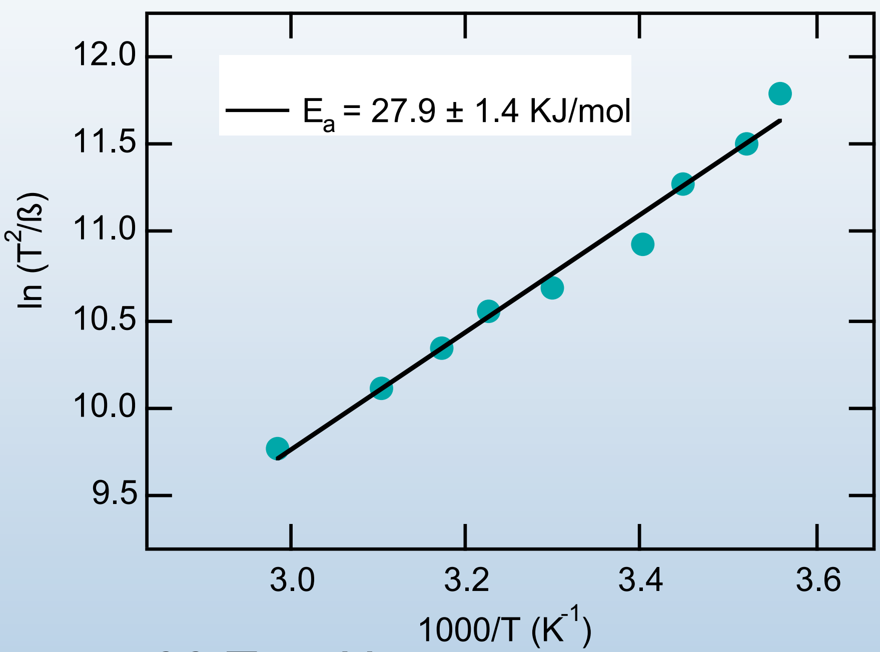


Normal Dose: Degas 825 K in vacuum, 500 Torr H_2 at room temperature

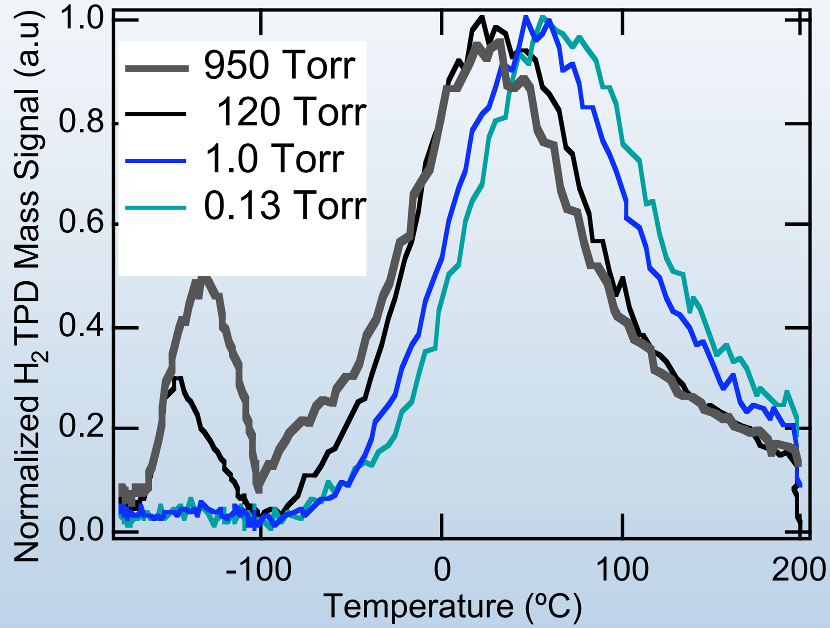
Reduction: Anneal to 775 K in 100 Torr H_2 for 10 min., Degas 825 K in vacuum, 500 Torr H_2 at room temperature. **Increase capacity to ~ 0.035 wt%.**

Organomettalic, Solution Phase Synthesis

UV photolysis of Co_2CO_8 w SWNTs



500 Torr H_2 at room temperature

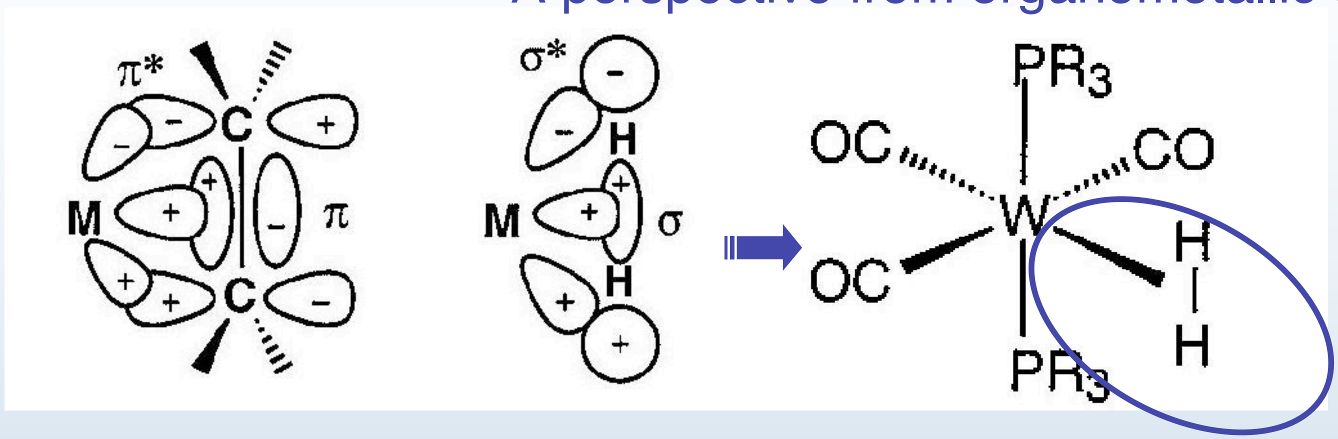


Shift to higher peak desorption temperature at low coverage.

Low capacity, but proof of concept

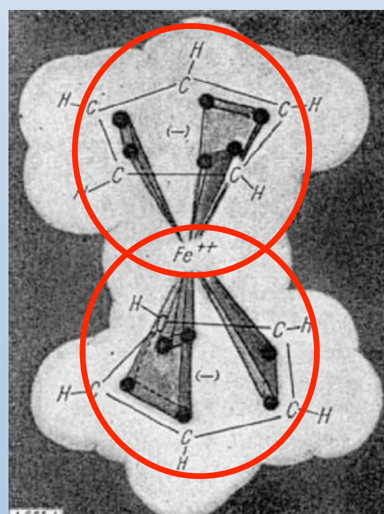
Approach: Rational Design of Adsorbents

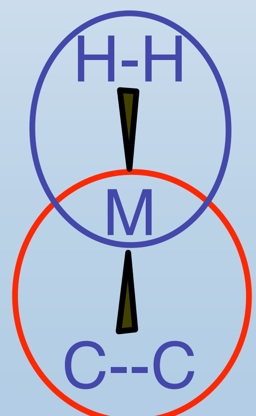
-- A perspective from organometallic chemistry



Kubas, J. Organometallic Chem. ***635****, 37 (2001)*

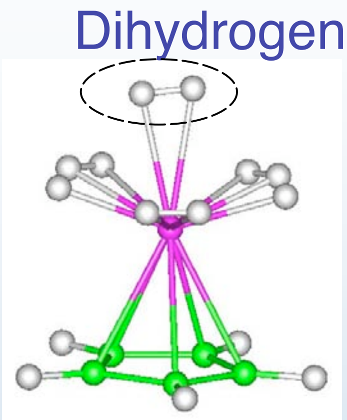
Fischer and Jira,
J. Organomet Chem.
637*, 7 (2001).*



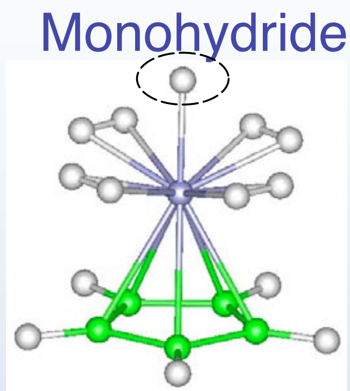


A new type of complex?

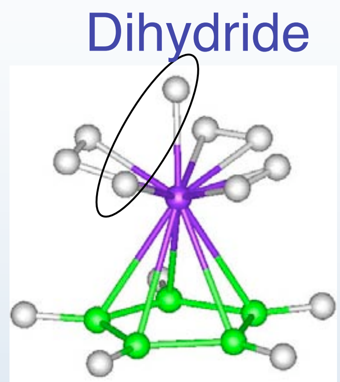
Calculated Structures of Hydrogen Saturated Cyclopentadiene (Cp) - [MHx] Complexes



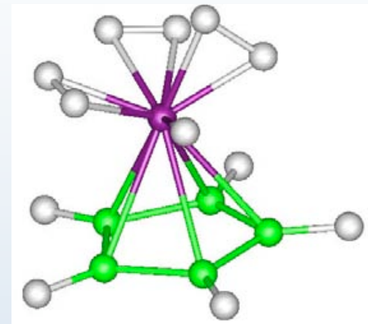
Sc



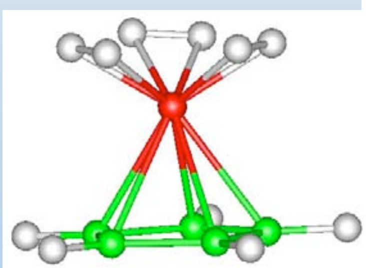
Ti



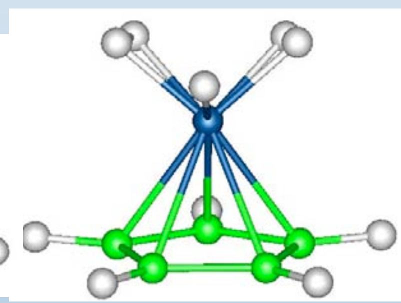
V



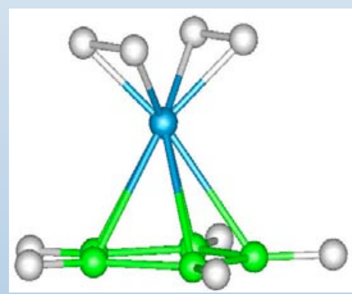
Cr



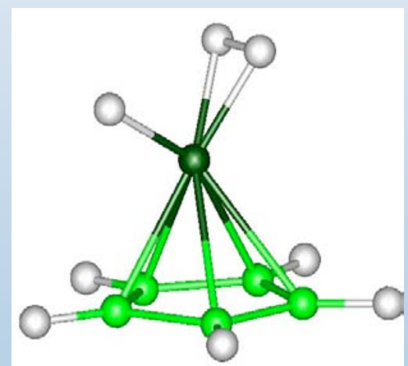
Mn



Fe



Co



Ni

Different H capacities for the different first row transition metals

18-e Rule and Cp-TM Binding

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
n_v N_H $E_b(kJ)$	**3** **10** **360**	**4** **9** **371**	5 8 333	6 7 221	7 6 258	8 5 285	9 4 314	10 3 389

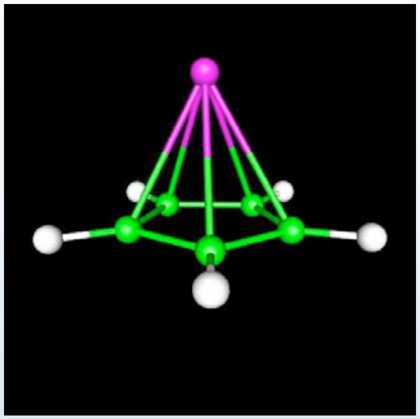
- 18-e rule: $n_v+N_H+5=18$

  n_v: number of valence electron in metal atom;
  N_H: number of hydrogen atoms bound;
  5: number of π electrons in the Cp ring.

- Sc binding to Cp: second largest E_b.

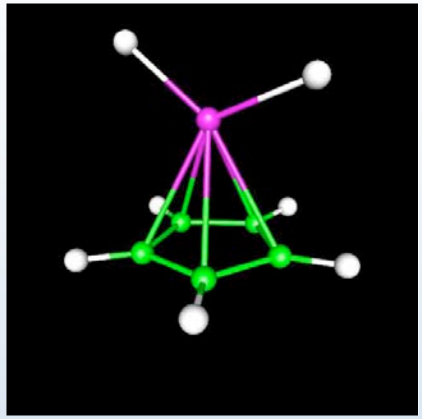
Reversible 6.7 wt% Storage

Stable “host”’ material



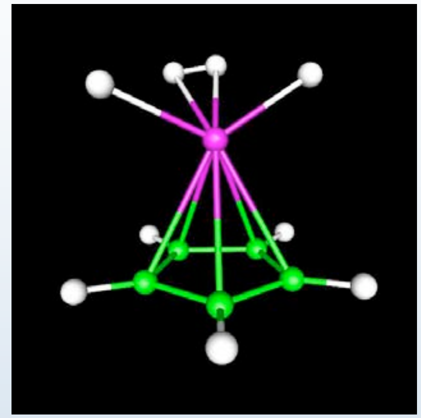
CpSc

+ H_2
124 kJ



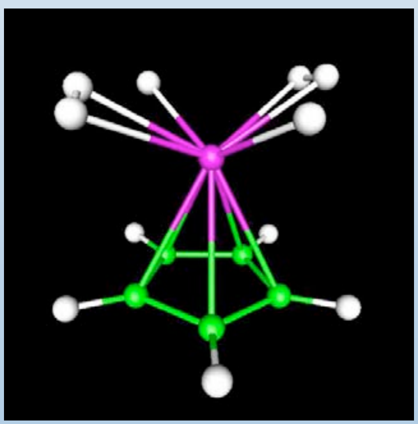
$Cp[ScH_2]$

+ H_2
30 kJ



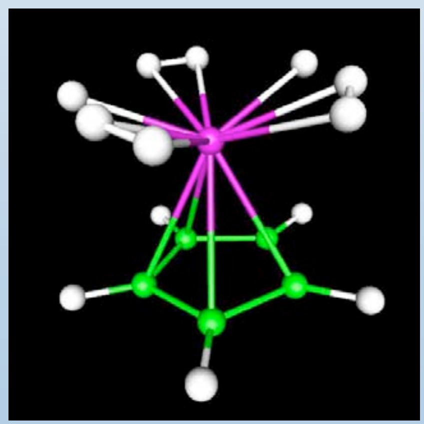
$Cp[ScH_2(H_2)]$

+ H_2
27 kJ



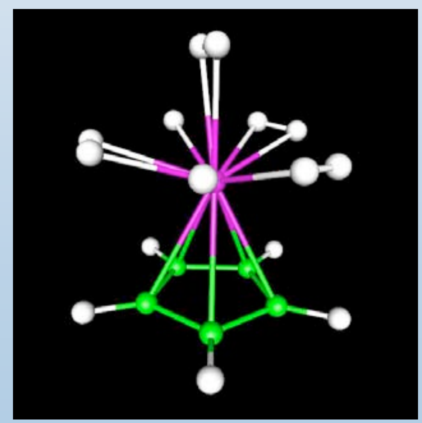
$Cp[ScH_2(H_2)_2]$

+ H_2
44 kJ



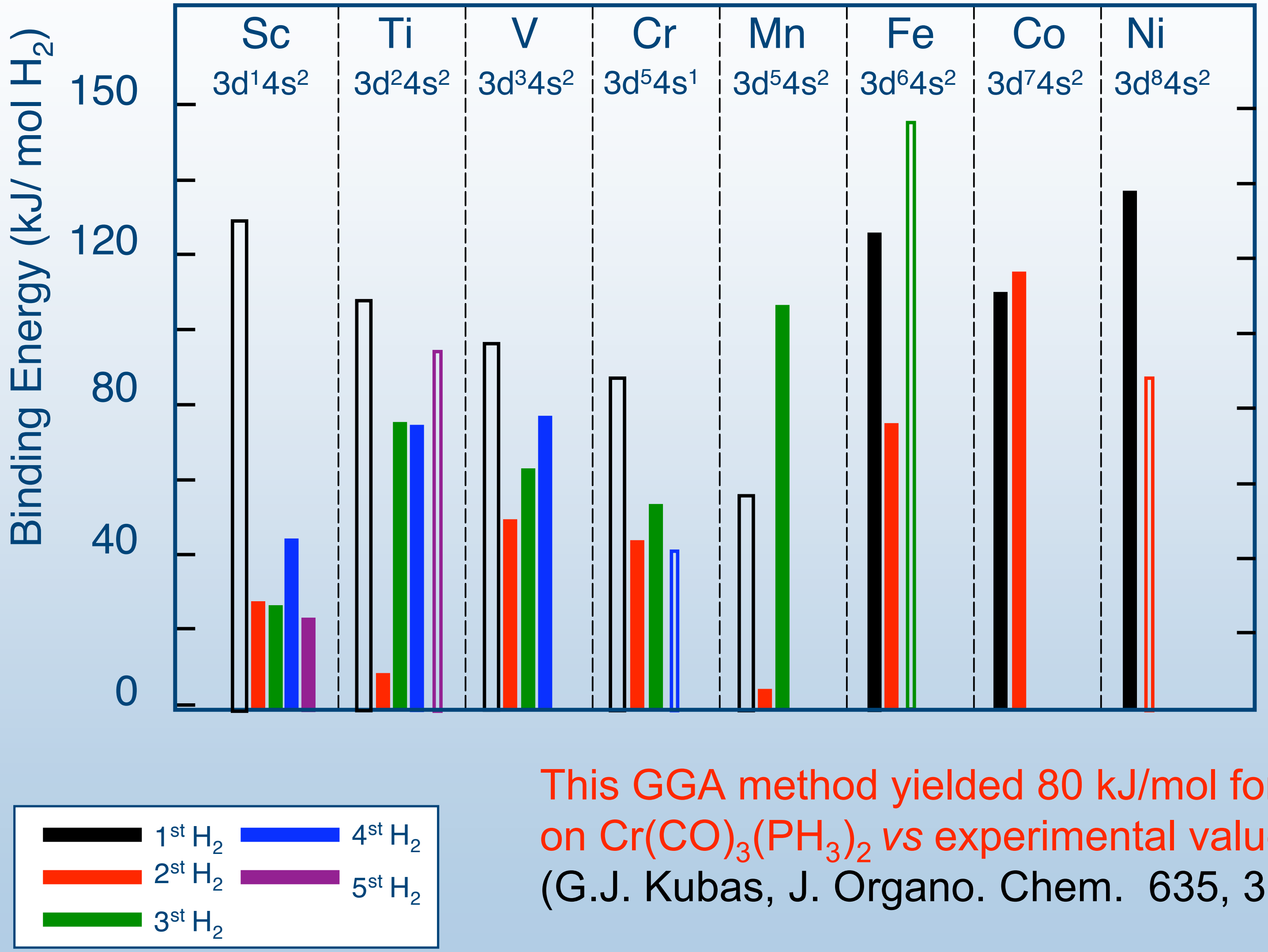
$Cp[ScH_2(H_2)_3]$

+ H_2
22 kJ



$Cp[ScH_2(H_2)_4]$

Energetics of Cp:TM-H_2 Binding



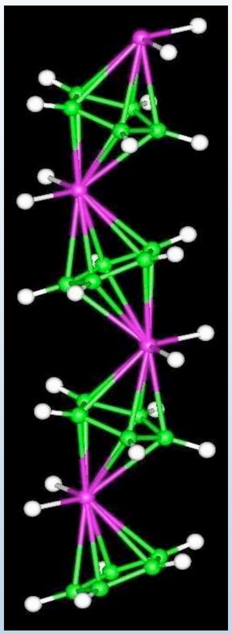
H-H bond length (Å)

Sc	4 x 0.80
Ti	4 x 0.85
V	3 x 0.9
Cr	3 x 0.96
Mn	3 x 0.94
Fe	2 x 0.95
Co	2 x 1.10
Ni	1 x 0.94

This GGA method yielded 80 kJ/mol for H_2 binding on $Cr(CO)_3(PH_3)_2$ *vs* experimental value 71 kJ/mol (G.J. Kubas, J. Organo. Chem. 635, 37, 2001)

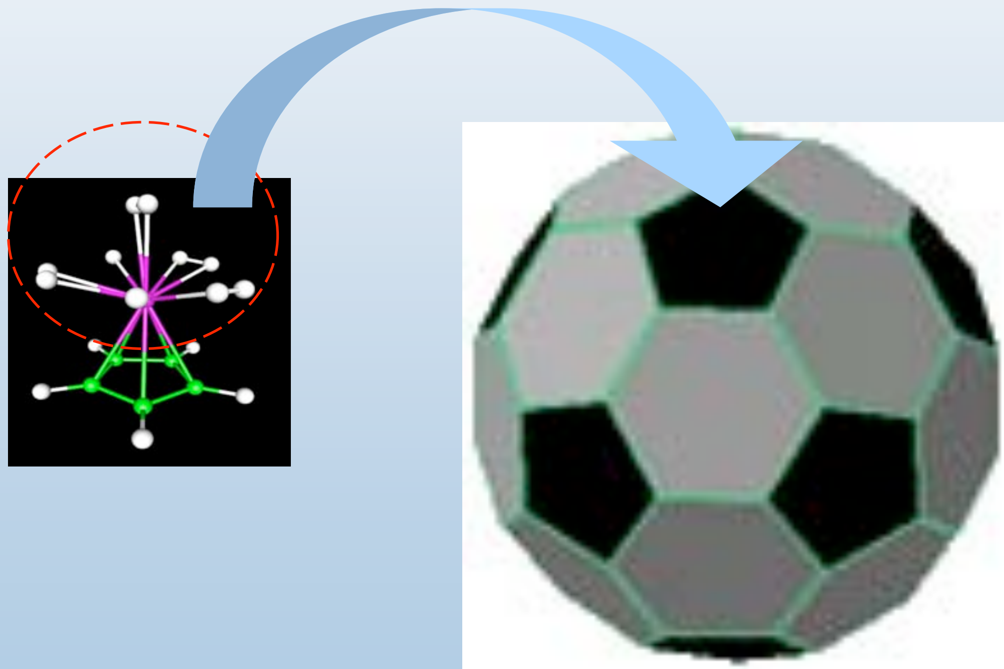
Integration with Carbon Frameworks

To avoid polymerization…..

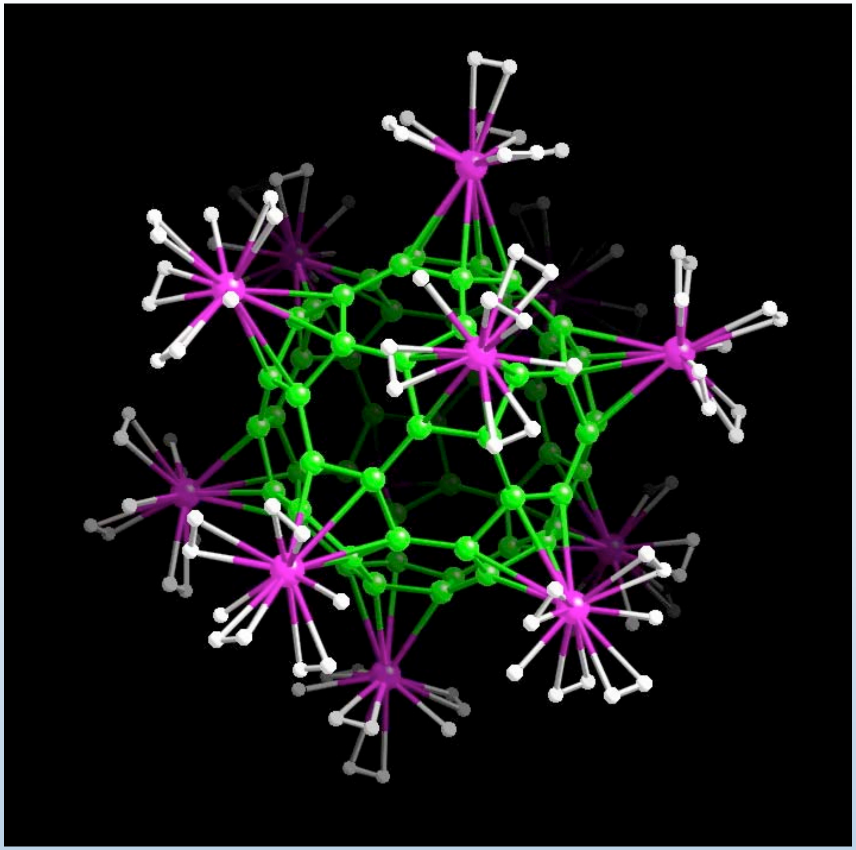


$Cp[ScH_2]$ chain

…transfer TM:H cluster to carbon framework (i.e. the pentagons of C_{60})



Route to 7 wt% Reversible Storage with Carbon-based Adsorbents



$C_{60}[ScH_2\,(H_2)_4]_{12}$

Metal-coated Fullerenes

Stable Scandium organo-metallic complex represents a compound that stores a total amount of hydrogen at 8.7 wt%, 7.0 wt% reversibly.

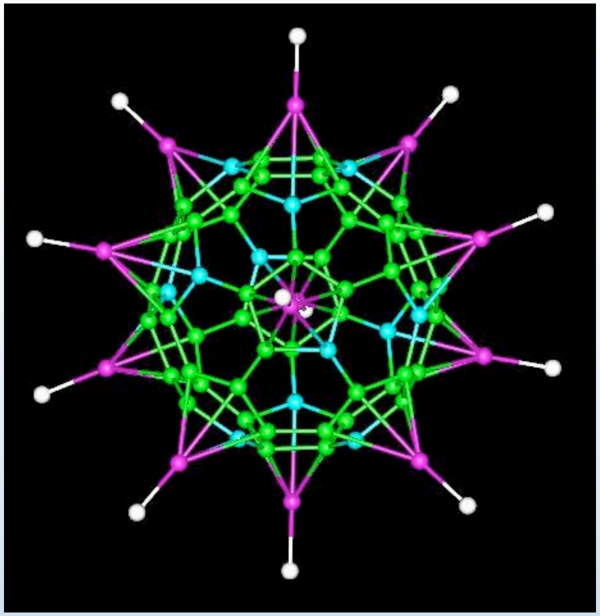
Minimum Energy Structure **with regions around the 5-membered rings that have aromatic character.**

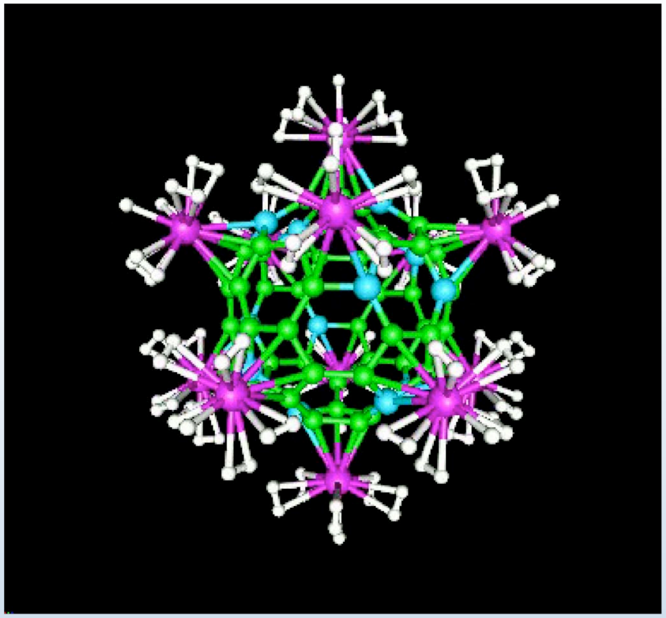
Without TMs, C_{60} has aromatic character around the 6-membered rings.

J. Poater, M. Duran and M. Sola Int. J. Quant. Chem. 98 (2004) 361

Y. Zhao, Y.-H. Kim, A.C. Dillon, M.J. Heben and S.B. Zhang PRL (in press)

Route to 8.8 wt% Reversible Storage with B-doped C_{60}



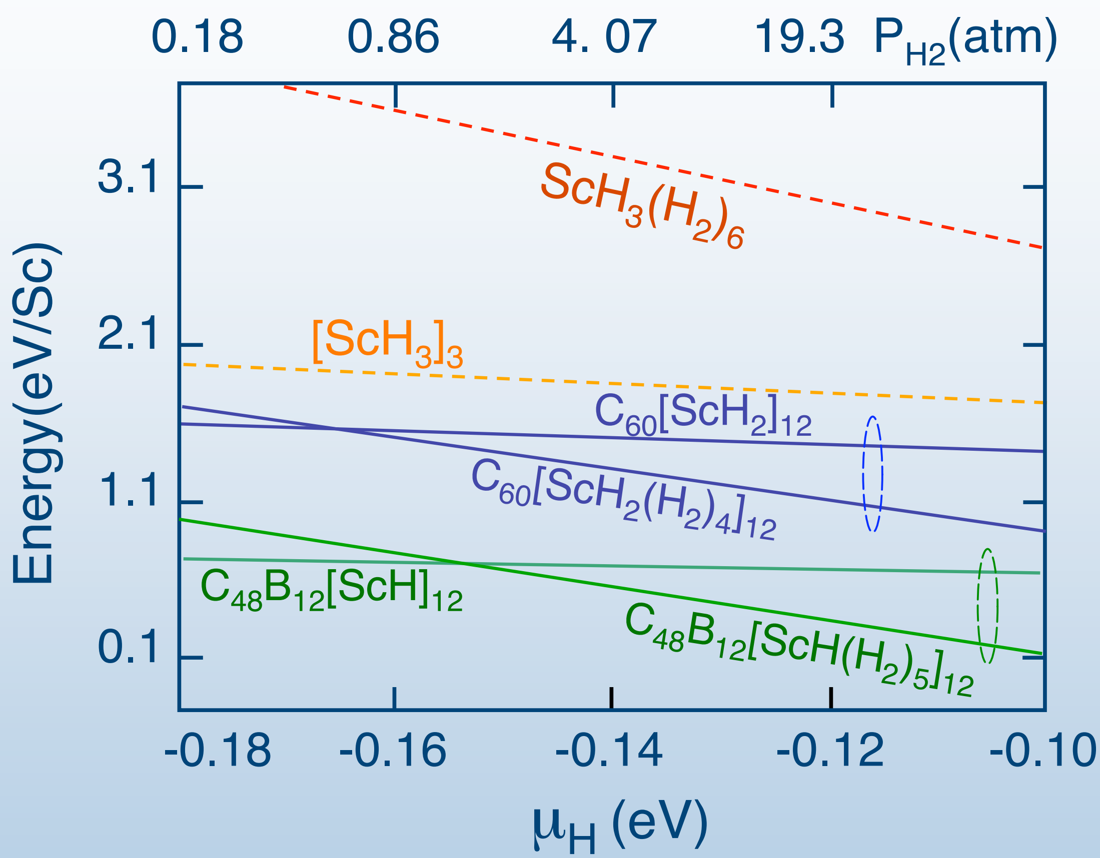


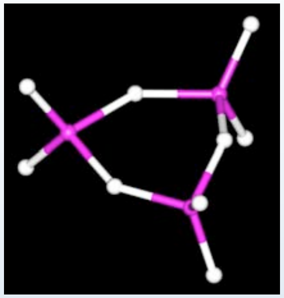
$$C_{48}B_{12}[ScH]_{12} \underset{}{\overset{60H_2}{\rightleftharpoons}} C_{48}B_{12}[ScH(H_2)_5]_{12}$$

One more electron transferred from a Sc to the pentagon

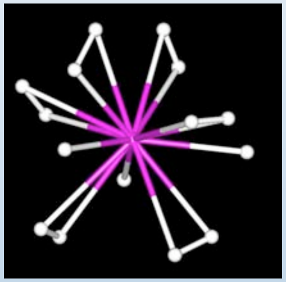
a) Enhanced Sc-C_{60} binding; b) Increased capacity;
c) 43 kg H_2/m^3 without efficient packing (conformal)

Reversible Storage at Room Temperature





$Sc[H_3(H_2)_6]$

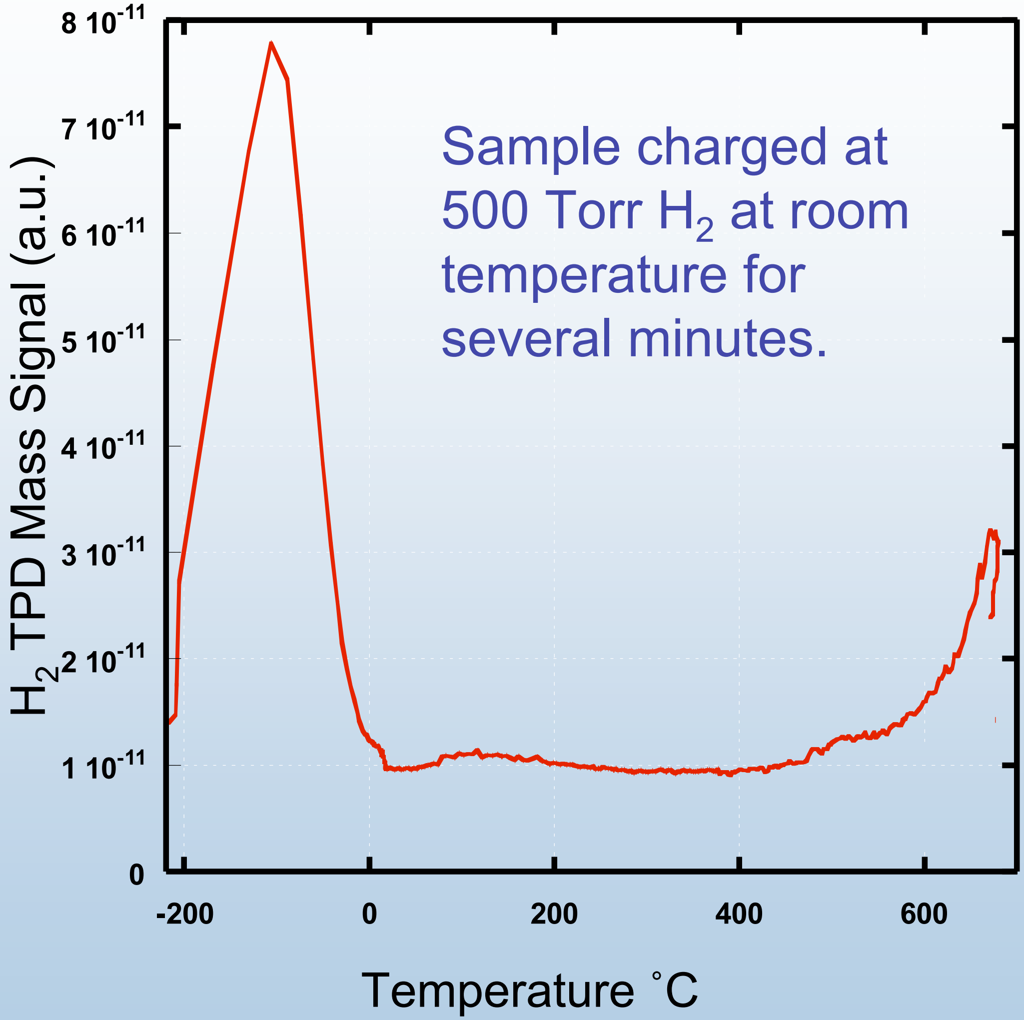


$[ScH_3]_3$

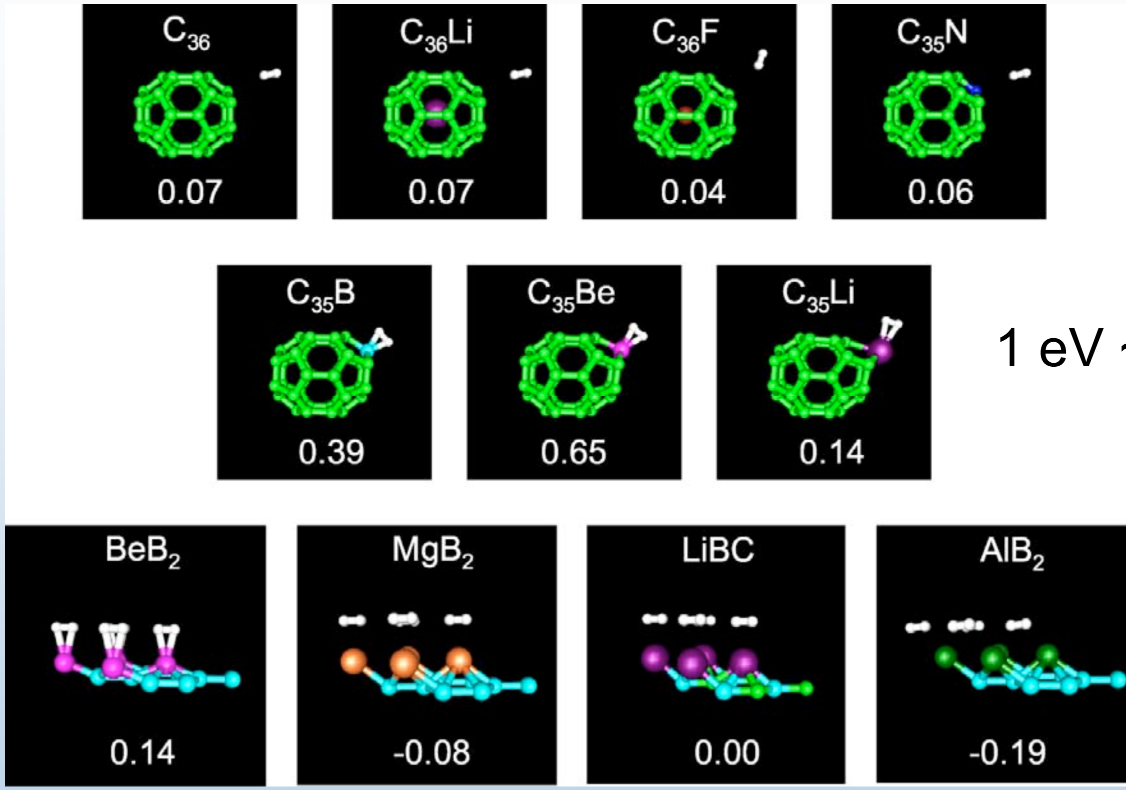
- Charge/release is switched at ~ 1 atm, T=300K;
- Storage materials are stable

Preliminary Data on an Sc / Carbon System

- Laser vaporization of graphite target doped with Cp_3Sc
- Enhanced low temperature adsorption peak
- Capacity must be evaluated with overpressure



Substitutional Doping: DFT within Local Density Approximation



1 eV ~ 100 kJ/mol

- LDA typically overbinds, whereas GGA typically under binds
- MP2 study showed LDA results are significantly closer[1]
- State-of-the-art fixed node, diffusion quantum Monte Carlo (QMC) calculations, performed by A. Williamson (LLNL), agrees

[1]Y. Okamoto et al., J. Phys. Chem. B 105, 3470 (2001).

Synthesizing Boron-doped Nanostructures

CVD

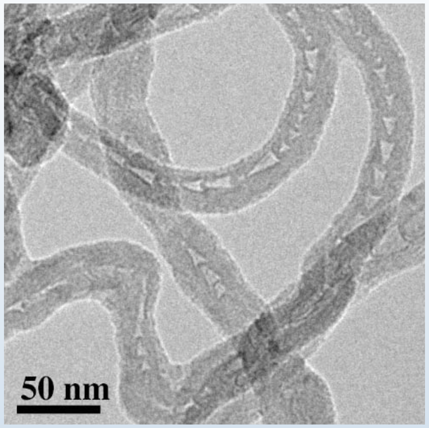
- Sources
  - $(C_6H_5)_3B$
  - $(CH_3)_3N{\bullet}BH_3$
  - $(CH_3)_3B_3O_3$
- HWCVD
  - Decomp. Of B source and ferrocene
- CVD
  - Decomp. Of B source over Fe-Mo catalysts

Laser and Arc

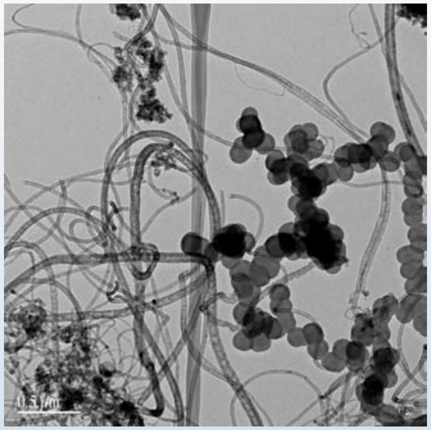
- Laser ablation dopants
  - B: low yield NTs
  - BN: low yield NTs
  - B_4C: low yield NTs
  - Gas phase dopants: onions and MW cages
  - high yield SWNTs with certain catalysts
- Arc dopants
  - High yield SWNTs with certain catalysts

Adsorption on B-doped Nanostructures

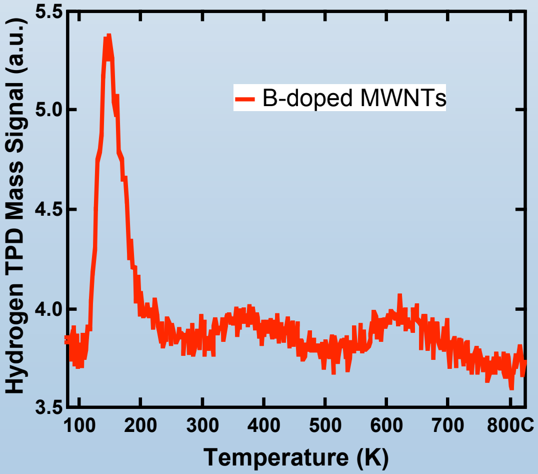
Bamboo-like MWNTs from HWCVD

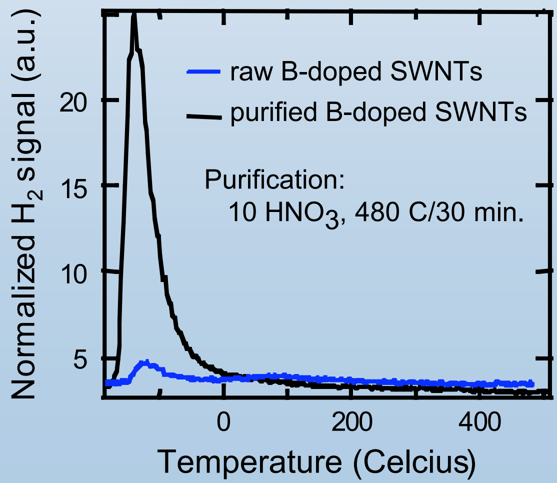


Conventional CVD using $(CH_3)_3N{\bullet}BH_3$



TPD spectrum shows two high energy binding sites on MWNTs in addition to low-T adsorption



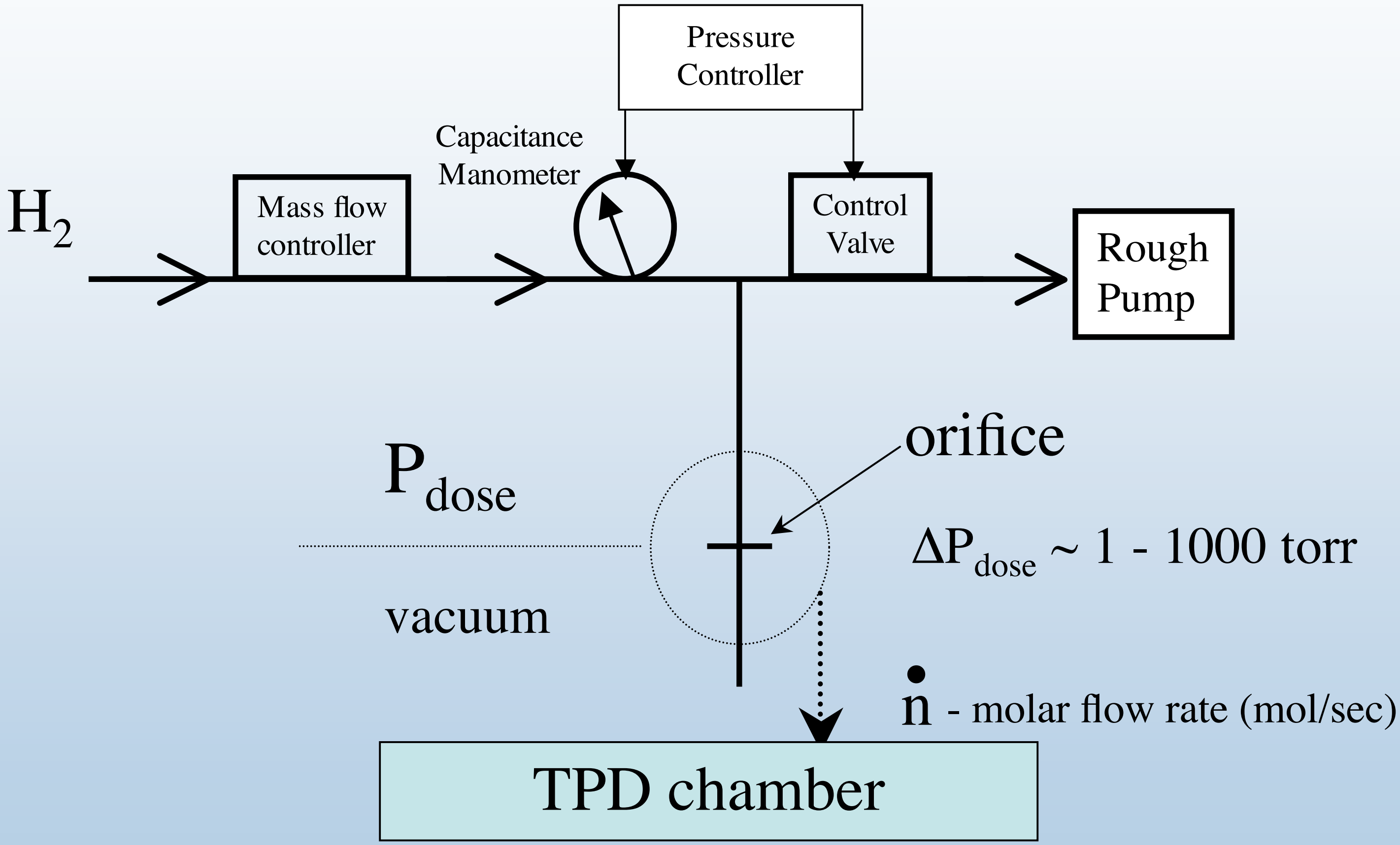


Increase in low-T adsorption in purified B-doped SWNTs

Capacity increse must be evaluated with overpressure.

Advances in Measurement Techniques

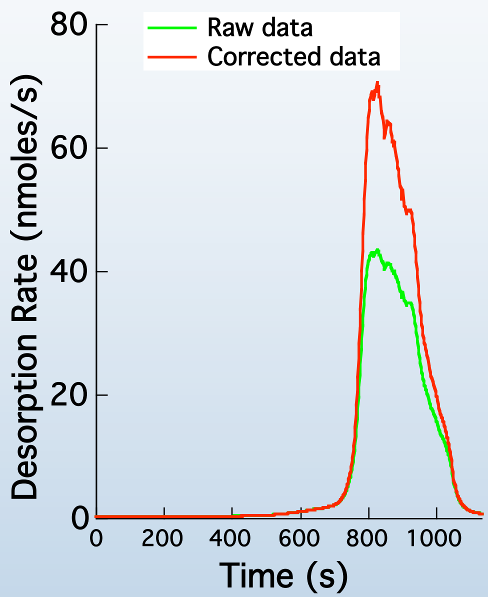
Variable Calibrated Leak for High Throughout, Quantitative TPD



Permits direct measurement of detector response as a function of molar flow rate ➜ accurate, *in situ* calibration

Using TiH_2 to Test Calibration

From SwRI/U. Penn review of NREL techniques

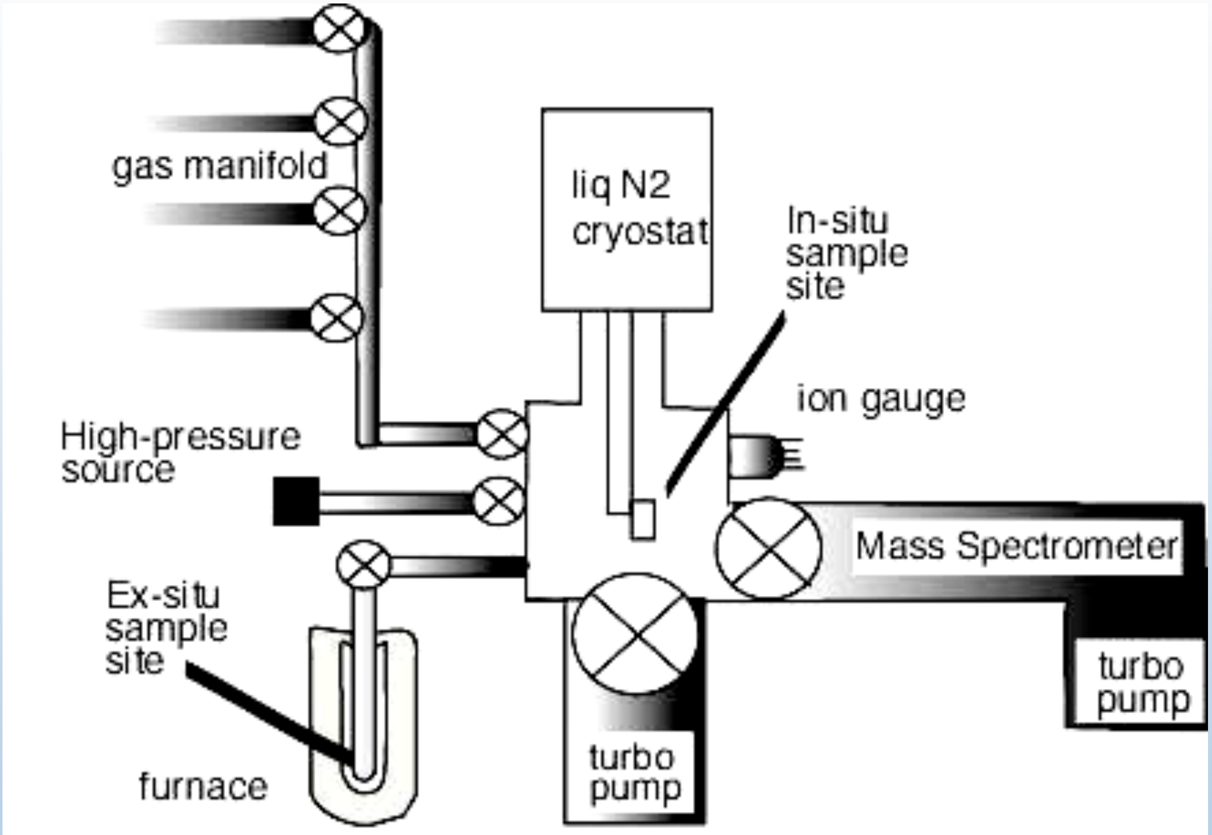


- Extends operation of detector into non-linear regime
- Accounts for detector aging
- 1 hr *vs.* several days
- Highly accurate
- Excellent agreement with volumetric measurements

Blind experiments showed calculation of the correct weight of TiH_2 with < 2% error

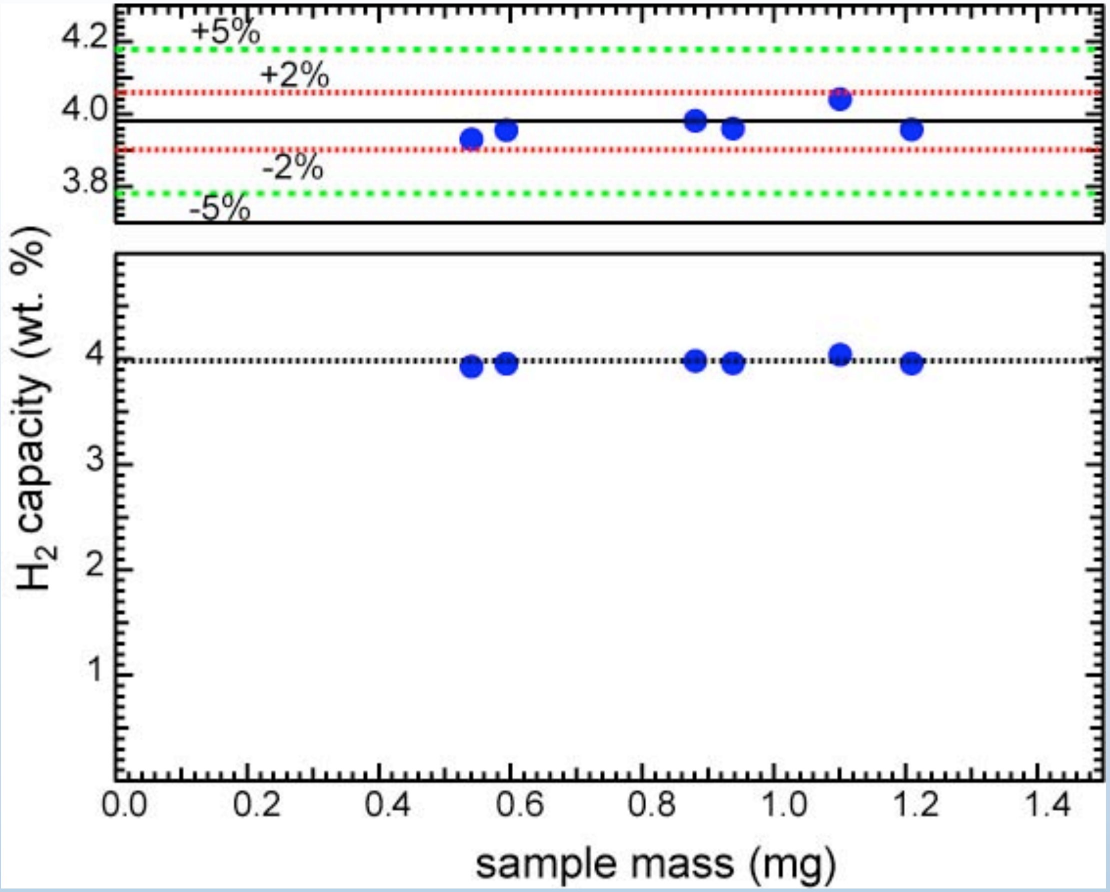
Loaded amount of TiH_2	Calculated Amount	Error
1.56 mg	1.54 mg	1.3 %
1.76 mg	1.73 mg	1.7 %

High Throughput Analysis with External Sample Cell



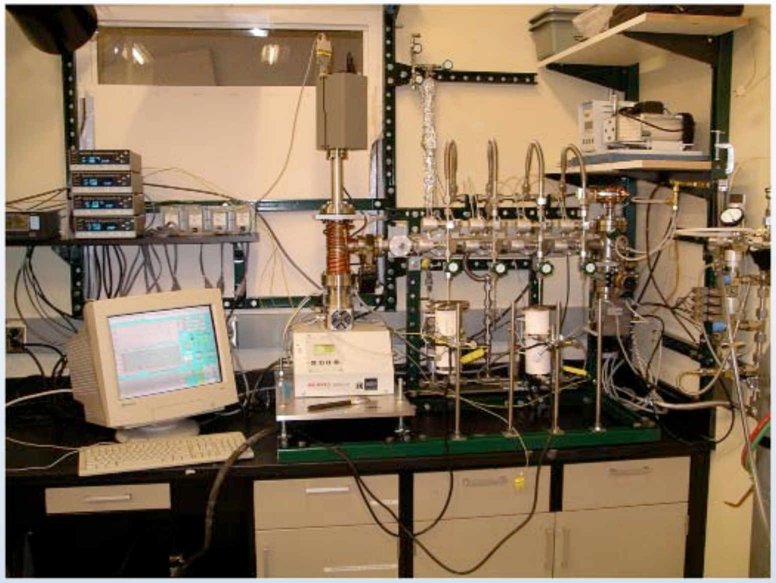
Multiple external cells can be connected to one manifold, with one mass spectrometer, for multi-sample, high throughput measurement

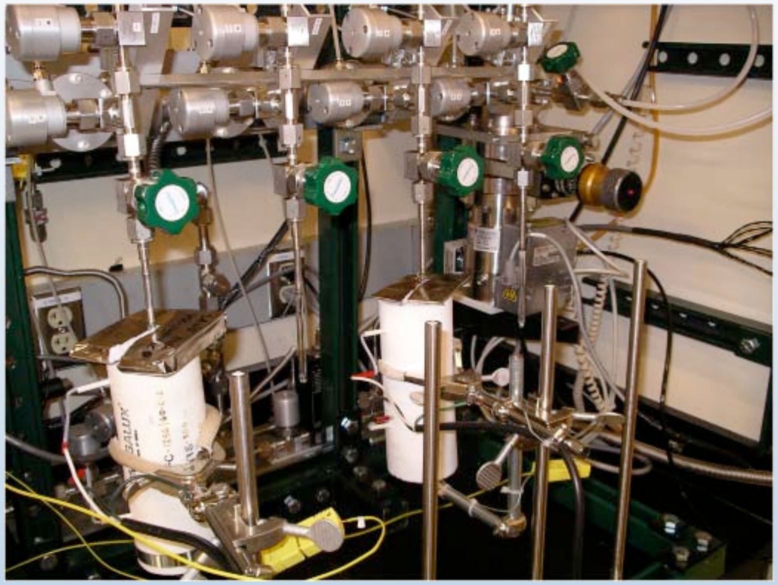
High Throughput, Accurate H_2 Measurement



Six samples of TiH_2 measured within 2% accuracy in 6 hours
Meets milestone (6 sample, within 5%, in 24 hrs)

High Throughput, Multi-station Apparatus



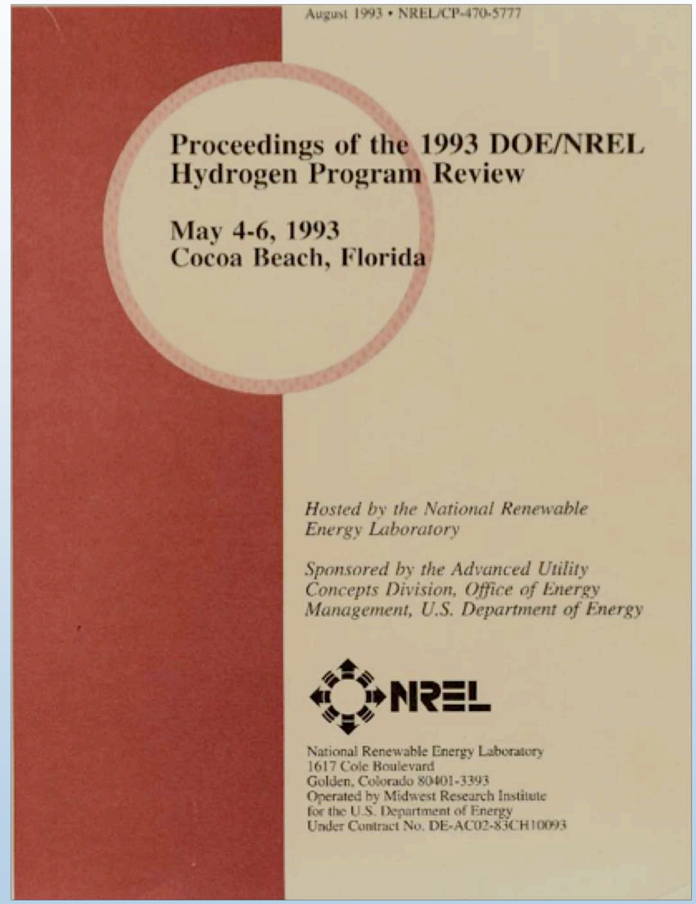


- *Current set-up has four stations and is expandable*
- *Will operate 24 hrs/day when fully automated*
- *Offers measurement support to Center partners*

Re-visiting Low T, Moderate P (< 100 bar) Adsorption Storage

"Activated carbon materials have been projected to meet and exceed …. density targets… if concurrent increases in hydrogen storage capacity and carbon density can be achieved. These two goals are in conflict for conventional porous materials such as activated carbons. However, the desired results may be obtained if the void spaces….can be organized … The synthesis of carbon nanotubules ….. indicate that such organization is possible."

in Proceedings of the 1993 DOE/NREL Hydrogen Program Review, pg 79.


August 1993 • NREL/CP-470-5777

Proceedings of the 1993 DOE/NREL
Hydrogen Program Review

May 4-6, 1993
Cocoa Beach, Florida

Hosted by the National Renewable Energy Laboratory

Sponsored by the Advanced Utility Concepts Division, Office of Energy Management, U.S. Department of Energy

NREL

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
Operated by Midwest Research Institute
for the U.S. Department of Energy
Under Contract No. DE-AC02-83CH10093

Re-visiting Low T, Moderate P (< 100 bar) Adsorption Storage

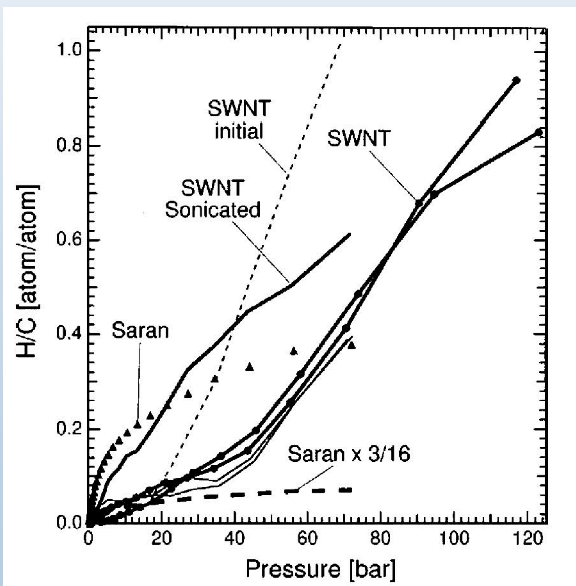
Seeking the "holy grail" for adsorbents:

Meeting DOE goals at ambient T and a few atmospheres

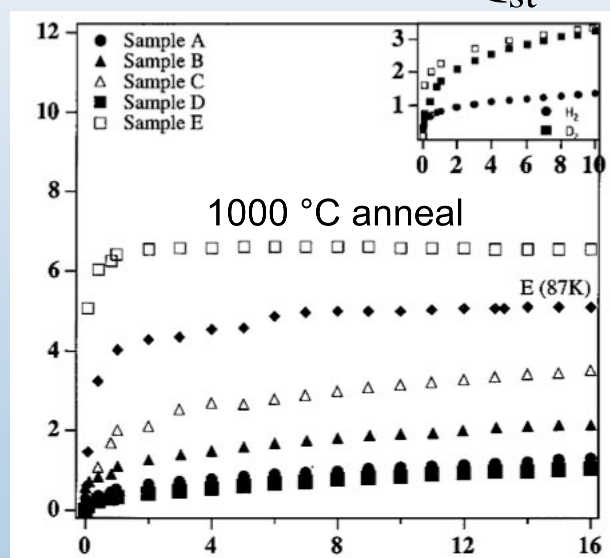
However:

Recent progress suggests that relaxing one (P or T) requirement can allow 2005 goals to be met

$Q_{st} \sim 0.12$ eV



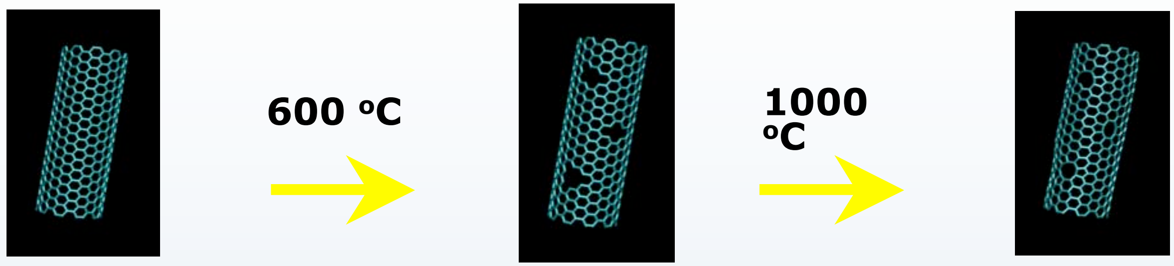
8 wt% on SWNTs at 80K, 100 bar
Ye, et al., APL 74, 2307 (1999)



6 wt% on SWNTs at 77K, 2 bar
Pradhan, et al., JMR **17**, 2209 (2002)

Courtesy of R. Chahine, UQTR

Hydrogen storage on SWNTs at 77 K and 1 bar



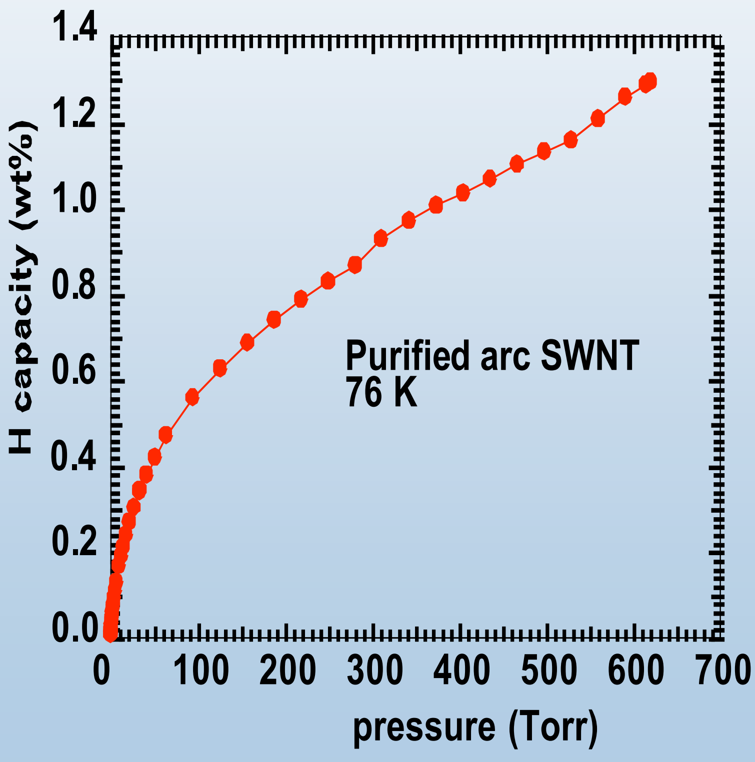
Acid	S_{spec} m^2/g	H_2 ads wt. %	S_{spec} m^2/g	H_2 ads wt. %	S_{spec} m^2/g	H_2 ads wt. %
HF	635	1,07	1555	4,6	806	1,73
HCl	878	1,55	1047	3,15	829	2,11
H_2SO_4	690	1,93	1084	1,38	430	1,12
HNO_3	40	1,04	375	0,98	193	1,22

- Both chemical and heat treatments result in an increase in the number and size of pores.

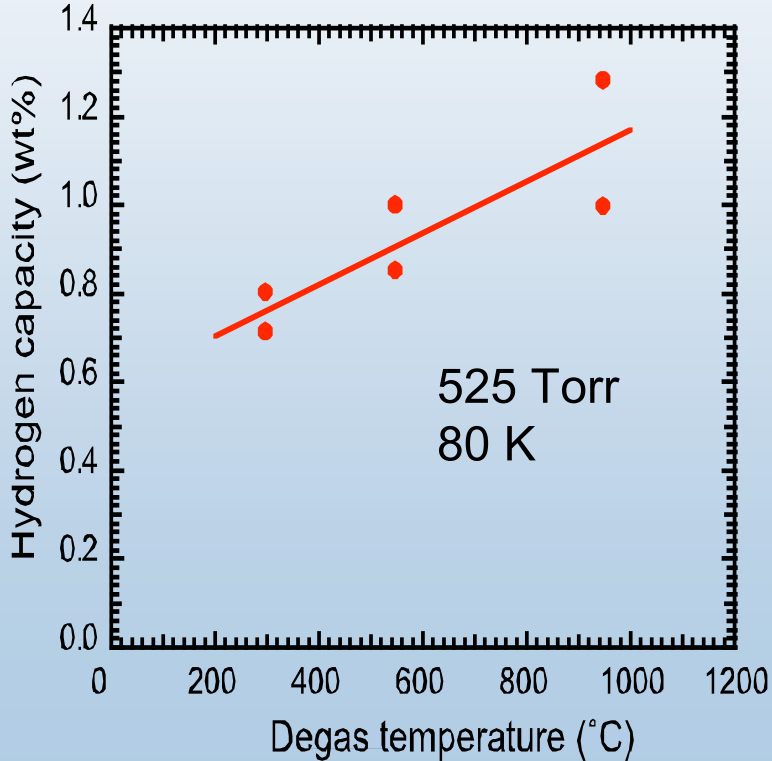
NREL Measurements at Low T, Low P

Purified arc-generated SWNTs

- *Isotherms with Quantochrome BET apparatus*
- *Single-point measurements in home-built volumetric*
- *Un-optimized materials*



Improvement with annealing

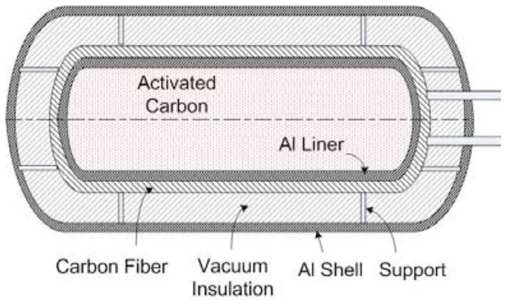


May have Potential to Meet 2005 System Targets

Preliminary System Analysis by Ramesh Ahluwalia, Argonne

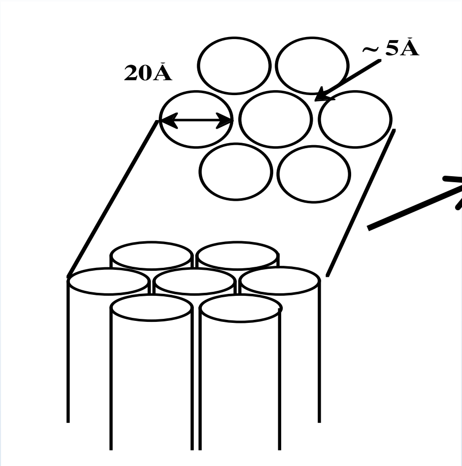
Engineered AC to Meet DOE-2005 Goals

- AX-21: Commercially available AC, 300 kg/m^3 bulk density
- Densified AX-21: 700 kg/m^3 bulk density
- EAC-05: Hypothetical AC engineered with physical properties to meet 2005 targets of 4.5 wt% and 36 kg/m^3.
- Development effort: 1 < 2 < 3 < 4 < 5 < 6.

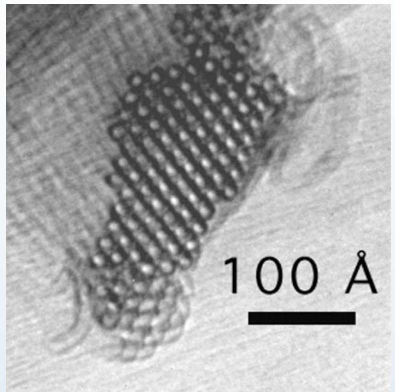


T	P	ΔT	AX-21		Densified AX-21		EAC-05	
(K)	(bar)	(K)	wt% H_2	kg/m^3	wt% H_2	kg/m^3	wt% H_2	kg/m^3
77	50	0	3.2	11.6	1.6	10.6		
77	50	50	5.0	19.5	3.2	23.0	4.5[2]	36
77	100	0	5.4	21.7	2.5	17.4		
77	100	50	7.1	29.6	4.1	29.9	4.5[1]	36
150	50	0	2.3	8.1	1.4	9.4	4.5[6]	36
150	50	50	2.8	10.0	1.8	12.4	4.5[5]	36
150	100	0	3.9	14.9	2.2	15.8	4.5[4]	36
150	100	50	4.3	16.8	2.6	18.8	4.5[3]	36

High Material Density for SWNT Arrays

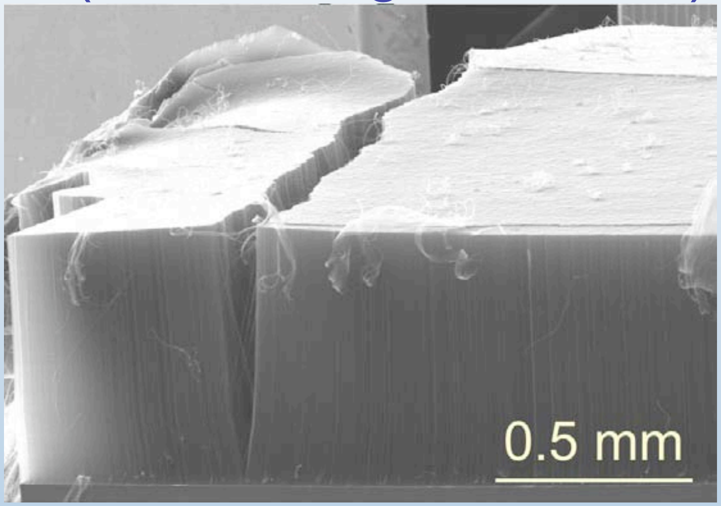


Concept in 1993



TEM in 2000

Macroscopic,vertically aligned arrays in 2005 (D. Geohegan, ORNL)



Can we achieve 6 - 8 wt% (80 K & 10 atm), with a bulk density approaching 1000 kg/m^3 (1 g/cc) ?

Potential winning technology

Comments from Last Year's Review

- 4 wt% capacity as a target is inadequate - should be revised to at least 8 wt% for any chance of success.
  - Interim target (FY2006) is 6 wt%
  - Developed rational approach to 8 wt% adsorbents
- Try to get industry involvement in collaborations.
  - Air Products and Chemicals, Inc., is leader in hydrogen technologies
  - Carbon Nanotechnologies, Inc., is leader in carbon nanomaterials
  - Connection through NREL's vehicle group connects the Center to numerous vehicle and vehicle component manufacturers
- Scope should be refocused beyond carbon nanotubes.
  - Scope now includes a wide variety of carbon-based materials

Comments from Review (cont.)

- Need to list what a system based on carbon materials would contain (including masses and volumes).
  - Work has begun to scope-out system from a thermal/fluid/mechanical & packaging point of view
  - Collaborating with Argonne (R. Ahluwalia)
- Cost needs to be assessed.
  - Analysis effort has begun with M. Mann & M. Ringer at NREL
  - Will be active with Tiax effort
  - Will build from cost estimate of scale-up of SWNT production previously done by NREL using input from industry (APCI, CNL and others)
- Focus totally on making a sample others can measure 4% storage in.
  - This *is* the main focus
- Cryo work is an appropriate addition.
  - Have expanded work in this area
- Key milestone is 4 wt% at external lab (SwRI) by Oct. 2005.

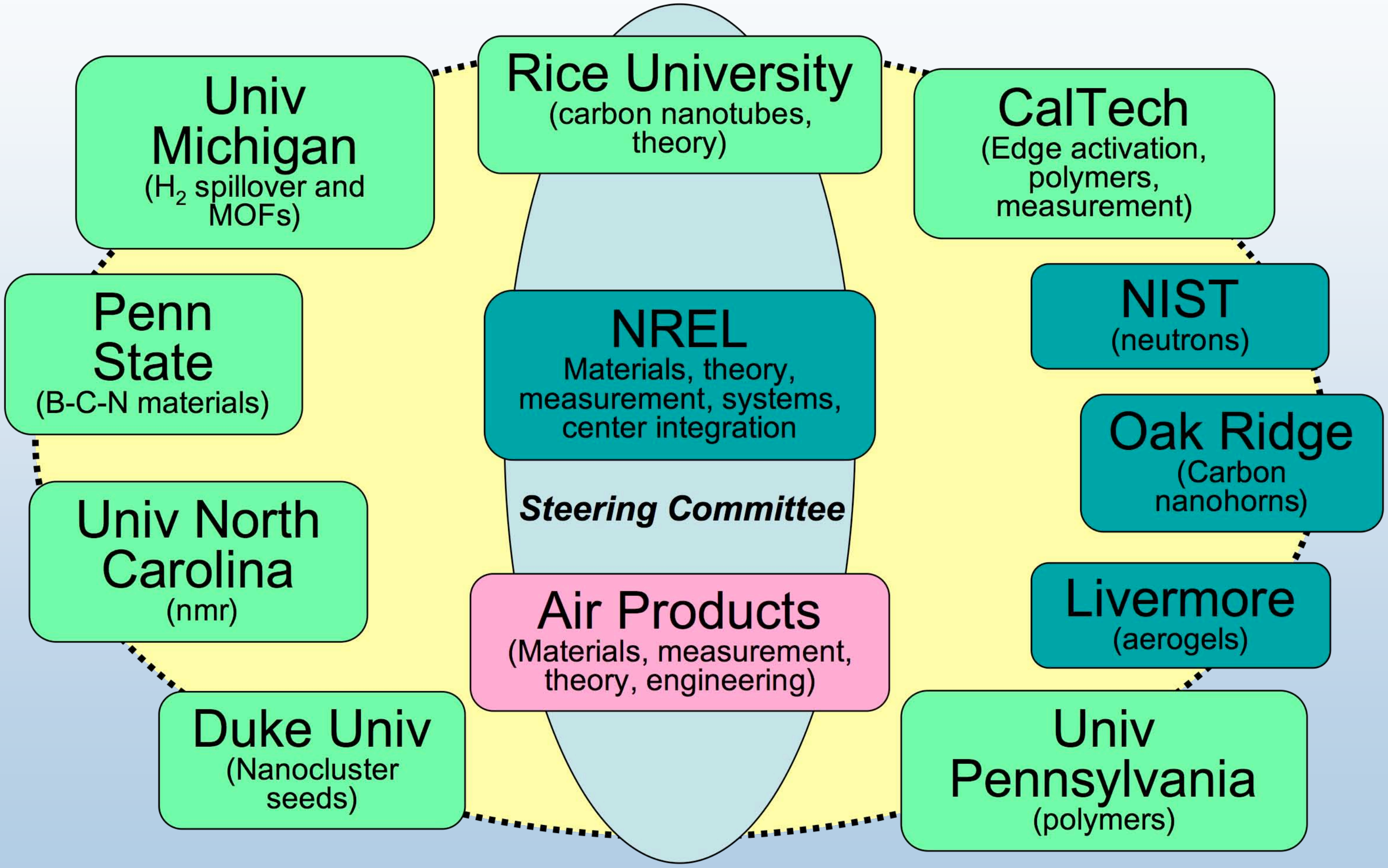
NREL Publications

1. "Non-dissociative adsorption of H_2 molecules in light-element doped fullerenes", Y.-H. Kim, Y. Zhao, A. Williamson, M.J. Heben, and S. B. Zhang, submitted to *Physical Review Letters*.
2. "Hydrogen storage in novel organometallic bucky balls", Y. Zhao, Y.-H. Kim, A.C. Dillon, M.J. Heben, and S. B. Zhang, to appear in *Physical Review Letters.*
3. "Experimental Gibbs free energy considerations in the nucleation and growth of single walled carbon nanotubes", L.M. Wagg, G.L. Hornyak, L. Grigorian, A.C. Dillon, K.M. Jones, J.L. Blackburn, P.A. Parilla and M.J. Heben, to appear in *J. Phys. Chem. B*
4. "Systematic inclusion of defects in pure carbon single-wall nanotubes and their effect on the Raman D-band" A.C. Dillon, P.A. Parilla, J.L. Alleman, T. Gennett, K.M. Jones & M.J. Heben. *Chemical Physics Letters* 401, 522-528 (2005).
5. "Generalized Kubas complexes as a novel means for room temperature molecular hydrogen storage", Y.-H. Kim, Y. Zhao, M. J. Heben, and S. B. Zhang, to be published in Hydrogen Storage Materials (Materials Research Society Symposium Proceedings).
6. "Discovering the mechanism of hydrogen adsorption on aromatic carbon nanostructures to develop adsorbents for vehicular applications", Y. Zhao, Y.-H. Kim, S. B. Zhang, J.L. Blackburn, A.C. Dillon, P.A. Parilla, A.H. Mahan, J.L. Alleman, K. M. Jones, T. Gennett, K.E.H. Gilbert, Y-W. Lee, B.M. Clemens and M.J. Heben, to be published in Hydrogen Storage Materials (Materials Research Society Symposium Proceedings).
7. "Hydrogen adsorption properties of single wall carbon nanotube-organometallic hybrid materials", T. Gennett, C. Curtis, J.L. Blackburn, K.M. Jones, J.L. Alleman, A.C. Dillon, M.J. Heben, to be published in Hydrogen Storage Materials (Materials Research Society Symposium Proceedings).
8. "Employing Raman spectroscopy to qualitatively evaluate the purity of carbon single-wall nanotube materials" A.C. Dillon, M. Yudasaka & M.S. Dresselhaus. *Journal of Nanoscience and Nanotechnology* 4, 691-703 (2004).
9. "High yield nanotube synthesis in a hot-zone arc-discharge apparatus", T. Gennett, C. Engtrakul, J. Blackburn, K. Franz, J. Alleman, K. Jones, A. Dillon, M. Heben, manuscript in preparation.
10. "Rapid, accurate, *in situ,* calibration of a mass spectrometer for temperature programmed desorption studies", K.E.H. Gilbert, P.A. Parilla, J.L. Blackburn, T. Gennett, A.C. Dillon, and M.J. Heben, manuscript in preparation.
11. "Competitive adsorption between carbon dioxide and methane on carbon nanotube materials" K.E.H. Gilbert, P.A. Parilla, J.L. Blackburn, T. Gennett, A.C. Dillon, and M.J. Heben, manuscript in preparation.
12. "Reaction intermediates in chemical vapor deposition growth of single-wall nanotubes", L.M. Wagg, J.L. Blackburn, A.C. Dillon, K.M. Jones, , P.A. Parilla and M.J. Heben, manuscript in preparation.
13. "Formation of nanooctahedra in molybdenum disulfide and molybdenum diselenide using pulsed laser vaporization", P.A. Parilla, A.C. Dillon, B.A. Parkinson, K.M. Jones, J. Alleman, G. Riker, D.S. Ginley & M.J. Heben. *Journal of Physical Chemistry B* 108, 6197-6207 (2004).
14. "High-energy, rechargeable Li-ion battery based on carbon nanotube technology", R.S. Morris, B.G. Dixon, T. Gennett, R. Raffaelle & M.J. Heben. *Journal of Power Sources* 138, 277-280 (2004).
15. "Development and characterization of single wall carbon nanotube Nafion actuators", B.J. Landi, R.P. Raffaelle, M.J. Heben, J.L. Alleman, W. VanDerveer & T. Gennett. to appear in *Materials Science and Engineering B*.

CbHS Center of Excellence Partners

9 university projects (at 7 universities), 4 government labs, 1 industrial partner

http://www.nrel.gov/basic_sciences/carbon_based_hydrogen_center.html



Themes of CbHS Center of Excellence

- Develop conducting and boron/carbon polymers, MOFs, carbon nanohorns, nanotubes and aerogels, and carbon-metal nanomaterials for on-vehicle storage
- Design and synthesize materials that bind hydrogen as either (i) weakly and reversibly bound atoms or (ii) as strongly bound molecules.
- Synthesize, test, develop light materials with high densities of appropriate binding sites per volume to meet DOE goals
- New concepts (e.g. conformal tanks with low T moderate P (<100 bar) operation, nanotube/hydride mixtures)

Center Organization

Steering Committee
- Air Products
- NREL
- Rice

Technical Director
NREL: Heben

Coordinator
Lin Simpson

Team 1: Materials Development Nanotubes, Fullerenes, and Nanohorns
- Air Products: Cooper — Activation
- Duke: Liu — Nanocluster Catalyst
- NREL: Dillon / Heben — Laser, arc, CVD, Activation
- Rice: Smalley — Cloning for growth of specific SWNTs
- ORNL: Geohegan — Carbon nanohorns

Team 2: Materials Development Other Nanostructures
- U Mich: Yaghi — Metal organic frameworks
- LLNL: Satcher — Metal/carbon aerogels
- Caltech: Ahn — Engineered dipole structures
- U Penn: MacDiarmid — Conducting Polymers
- Penn State: Eklund — B-C-N materials
- U Mich: Yang — Hydrogen spillover
- NREL: Dillon — Novel nanostructures by Hot-wire CVD

Team 3: Hydrogen Measurements
- NREL: Dillon — Mechanistic studies TPD, IR, Raman
- NIST: Neumann — Neutron spectroscopy, Prompt gamma analysis
- U North Carolina: Wu — Nuclear magnetic resonance
- Group Analysis — Volumetric, gravimetric, TPD
  - Penn State: Eklund
  - Caltech: Bowman
  - NREL: Parilla
  - U Mich: Yang
  - Air Products: Cooper
  - U Mich: Yaghi

Team 4: Predictive Theory
- Air Products: Cheng — Hydrogen interactions
- NREL: Zhang — Nanoscale environments
- Rice: Yakobson — SWNT interactions

Team 5: Systems, Analysis & External Connections
- Air Products: Pez — Systems Guidance
- NREL: Mann — Techno-economic analysis
- NREL: Wipke/Kelly — Vehicle Systems
- International Energy Agency, IPHE, Southwest Research Institute, Additional collaborations

Work Plan and Timeline

Materials Development & Characterization
Specific SWNTs, BCNs, nanohorns, GNFs, MOFs, polymers, carbon/metal hybrids, functionalization, activation

Focused Materials Development
Manufacturability

Hydrogen Measurements
NMR, neutrons, Raman, IR, volumetric, gravimetric, TPD, high-throughput

System Measurements
Capacity, kinetics, heat, safety
Impurity tolerance

Mechanistic & Predictive Theory

System Modeling
Techno-economic analysis

Systems, Techno-economic Analysis

1 kg H_2 System Construction

Down-select materials/mechanisms

3 yrs , basic & applied research, demonstrate feasibility of materials, understand dynamics & mechanisms

Material/Approach Go/No-Go

Center Go/No-Go

2 yrs, continued basic and applied research, technology development, system with 1 kg of available hydrogen.

Phase One | Phase Two

FY2005 FY2006 FY2007 FY2008 FY2009 FY2010

Designing Microporous Carbons for Hydrogen Storage Systems

carried out in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

Alan C. Cooper, Hansong Cheng, and Guido P. Pez

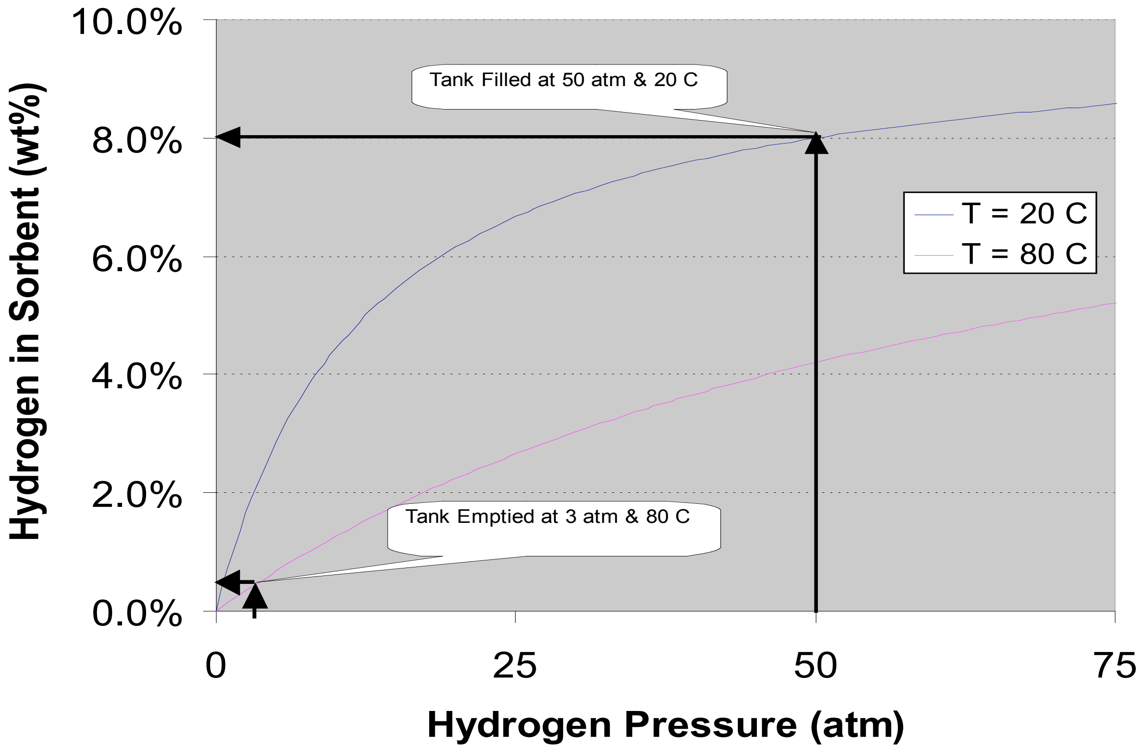
Air Products and Chemicals, Inc.

2005 DOE HFCIT Annual Program Review

STP-43

This presentation does not contain any proprietary or confidential information

Conceptual System Design: System Engineering Model of Adsorption



- Langmuir isotherm model assumes a Δ H of -25 kJ/mol and ΔS of -105 J/mol·K
- The "tank" can deliver 7.56 wt. % H_2 under these modeling conditions

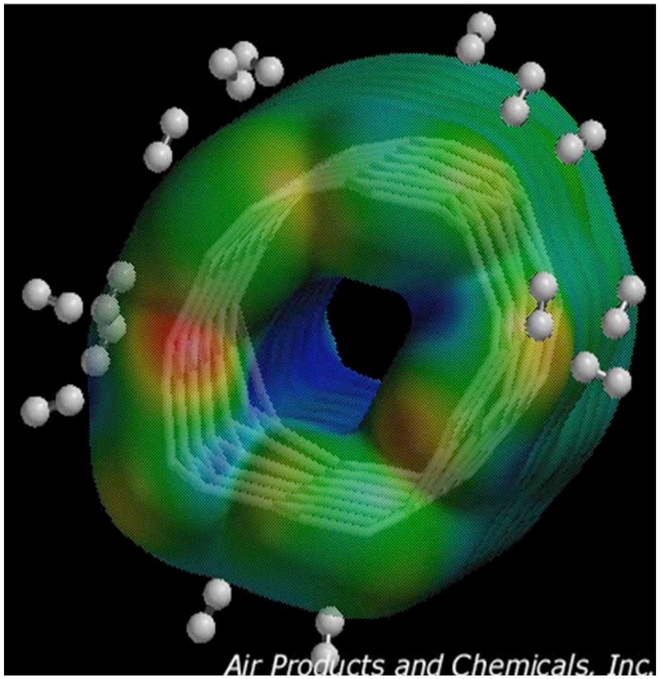
Gravimetric hydrogen capacity is linked to the heat (ΔH) and the entropy (ΔS) of H_2 sorption, which determine the strength and extent of equilibrium binding to the sorbent, and to the volumetric space per unit mass of sorbent that is accessible to hydrogen capture. The sorbent (S) and H_2 equilibrium is expressed as:

$$S(s) + H_2(g) \overset{K}{\rightleftharpoons} S\bullet H_2(s) \text{ where } K = [S\bullet H_2] / [S]P_{H_2} \quad (\text{atm}^{-1})$$

Computational Studies of Hydrogen Adsorption on Carbon-based Materials

- H_2 adsorption in carbon nanomaterials (nanotubes, nanohorns, nanofibers, etc.)
  - Objectives: study storage capacity at given pressure and temperature and identify material properties key to adsorption
  - Methods: NPT-MD, GCMC
  - Potential collaborators: Rice University, NREL

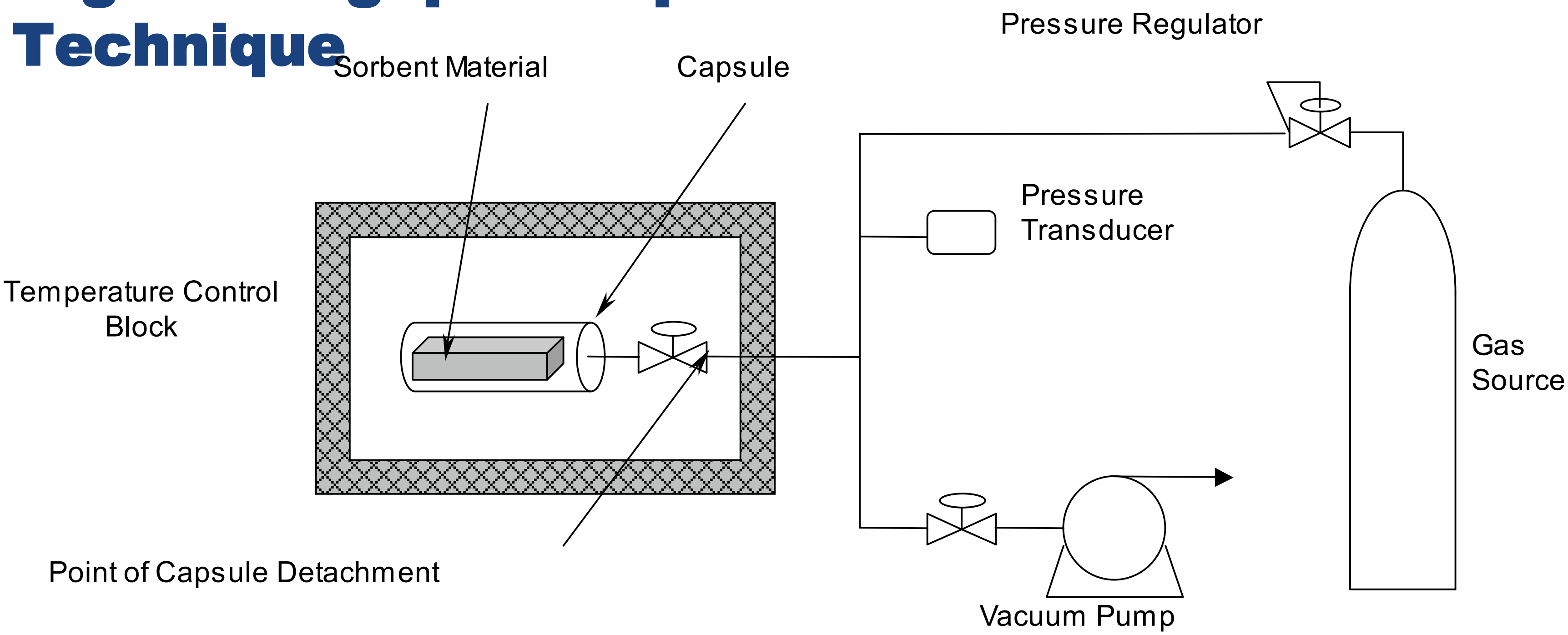
- H spillover onto carbon nanomaterials (nanofibers, nanotubes, etc.)
  - Objectives: evaluate energetics for H spillover, identify chemisorption pattern, kinetics
  - Methods: Monte Carlo, DFT, MD
  - Potential collaborators: Rice University U. of Michigan, NREL



Electrostatic potential mapped to the electron density of a deformed (5,5) singlewalled carbon nanotube

AIR PRODUCTS

Advanced Measurements of Hydrogen Adsorption: Exploration of a Novel Low-cost, High-throughput Sorption Measurement Technique



- Direct method that measures the total amount of hydrogen (sorbed + gaseous) stored in a pressurized vessel containing a sorbent
- Measurements can be performed at ambient to high temperatures and high hydrogen pressures
- Inexpensive technique (requires an accurate analytical balance)
- Potential for high throughput screening

CLONING SINGLE WALL CARBON NANOTUBES FOR HYDROGEN STORAGE

Richard E. Smalley
Carbon Nanotechnology Laboratory
Rice University

A Participant in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

May 23, 2005

DOE 2005 Hydrogen Program Annual Review
Washingtion, D.C., May 23, 2005

Project ID #

General Objectives:

Develop methods for producing type-selected SWNT

Produce particular SWNT types for hydrogen storage evaluation

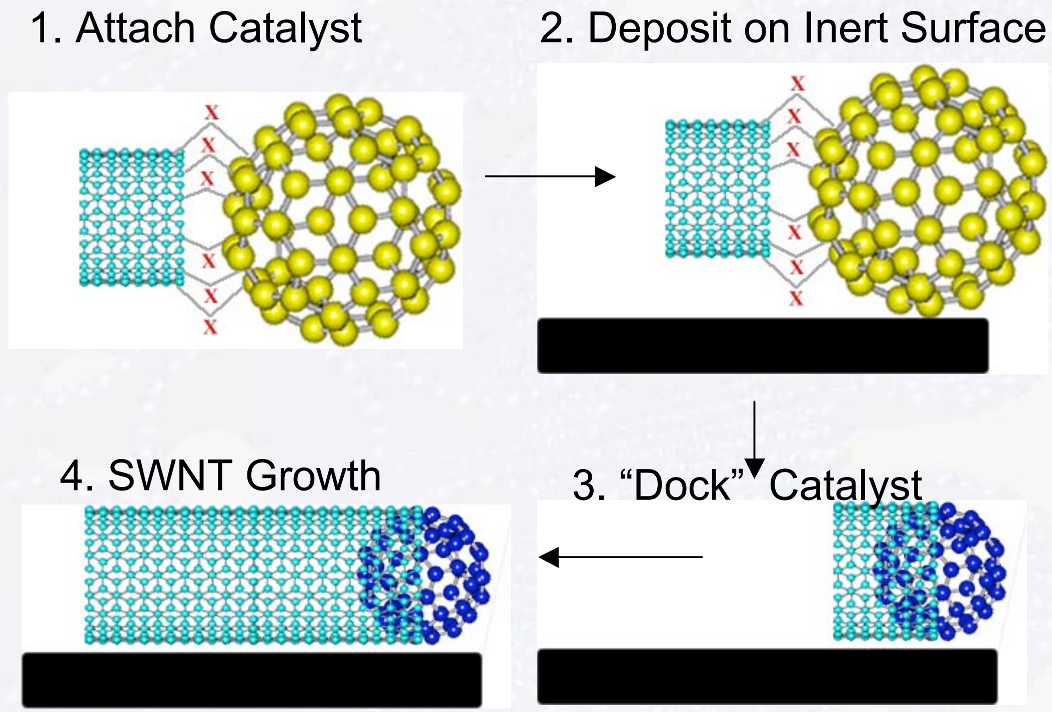
Scale production technology & deliver optimized SWNT material for prototype hydrogen storage system development

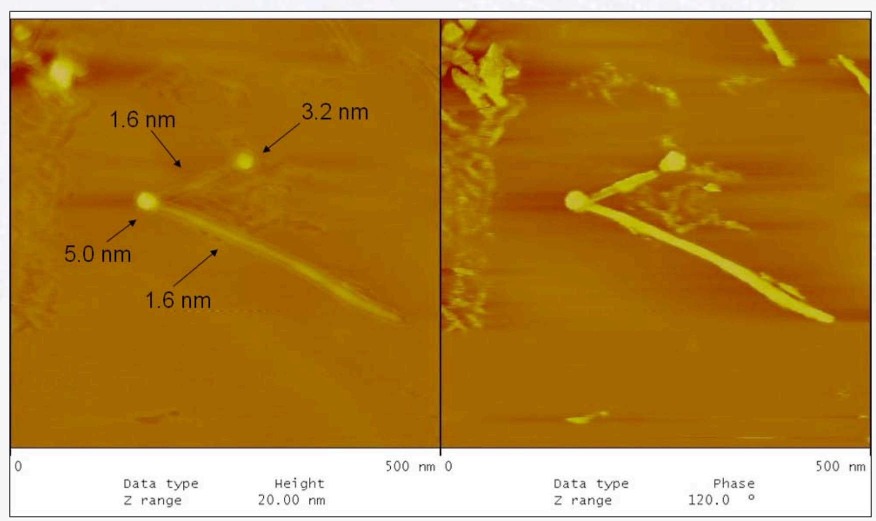
SWNT Seeded Growth

Current Results

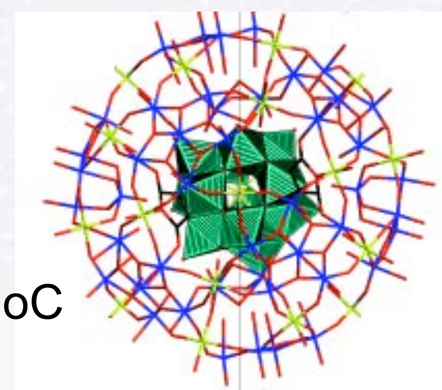
Key Starting Materials
- Have FeMoC Catalyst
- Have Short SWNT Seeds
- Have Soluble SWNT

Key Process Steps
- In-Solution Attachment
- Controlled Deposition
- Catalyst Docking
- Reductive Etching
- Limited Growth
- *Luxuriant Growth is Next !!*





FeMoC



Controlling the Diameter of Single Walled Carbon Nanotubes for Hydrogen Storage

-Carried in the “DOE Center pf Excellence on Carbon-Based Hydrogen Storage Materials”

Lei An and Jie Liu

Duke University

05/23/2005

This presentation does not contain any proprietary or confidential information

Project ID # STP35

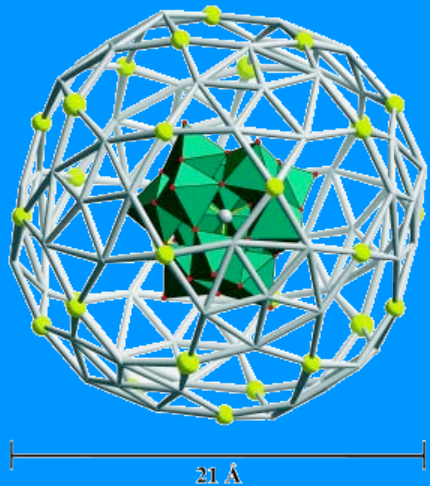
Approach 1: Using Molecular Cluster as Catalysts to Control the Diameters of SWNTs

Motivation:

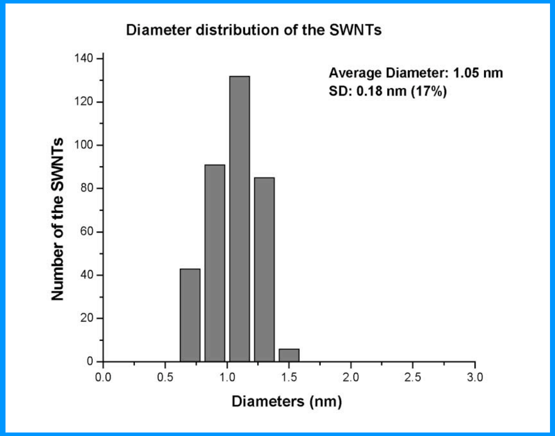
- The diameter of single walled carbon nanotubes is controlled by the size of catalyst nanoparticle during the initiation stage of the growth. If the diameter of the catalysts can be controlled, the diameter of the nanotubes can be controlled.
- Molecular clusters are molecules with identical number of metal atoms in each cluster, making them perfect catalysts for the growth of uniform nanotubes.
- The growth of uniform nanotubes were demonstrated before by our group using one type of clusters (Figures on the right).

Things to Do:

- Making smaller nanotubes using smaller cluster molecules (Next Page)
- Developing method to produce gram quantity of uniform nanotubes.



$[H_xPMo_{12}O_{40} \subset H_4Mo_{72}^{VI}Fe_{30}^{III}(CH_3COO)_{15}O_{254}(H_2O)_{98}].60H_2O$



L. An, J. M. Owens, L. E. McNeil, and J. Liu, *JACS*, **124**, 13688-13689, (2002).

Optimization of SWNT Production and Theoretical Models of H_2-SWNT Systems For Hydrogen Storage

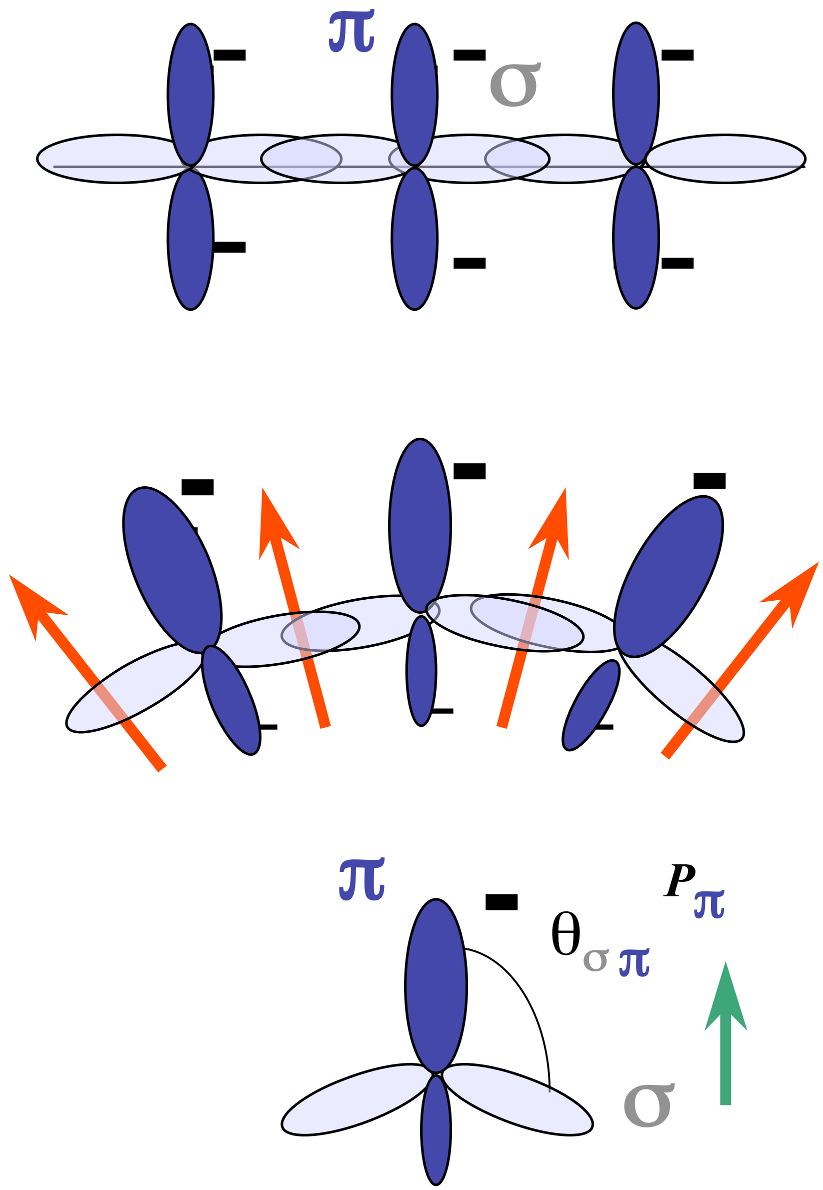
Carried out in the DOE Center of Excellence on Carbon-based Hydrogen Storage

Boris Yakobson and Robert Hauge

Rice University

May 25, 2005

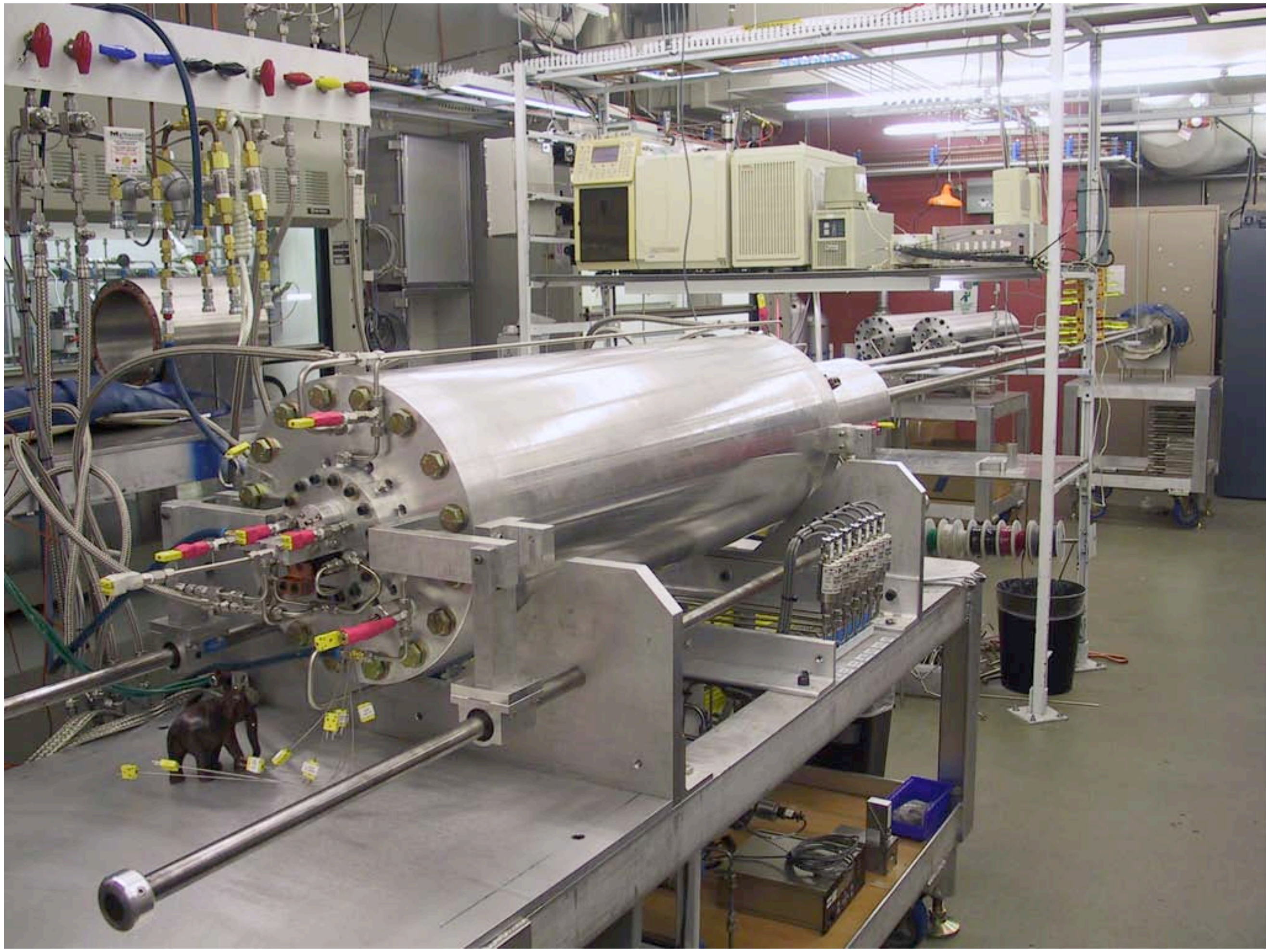
Project ID #STP38



Will further explore curvature-induced polarization and evaluate local field and their ability to change the energy of physisorption

Preliminary/past work
Yakobson *et al.*,
Chem Phys Lett v **360**, p 182

HiPco Reactor



Enhanced Hydrogen Dipole Physisorption

Channing Ahn, R. H. Grubbs and R. C. Bowman, Jr.
California Institute of Technology
with DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

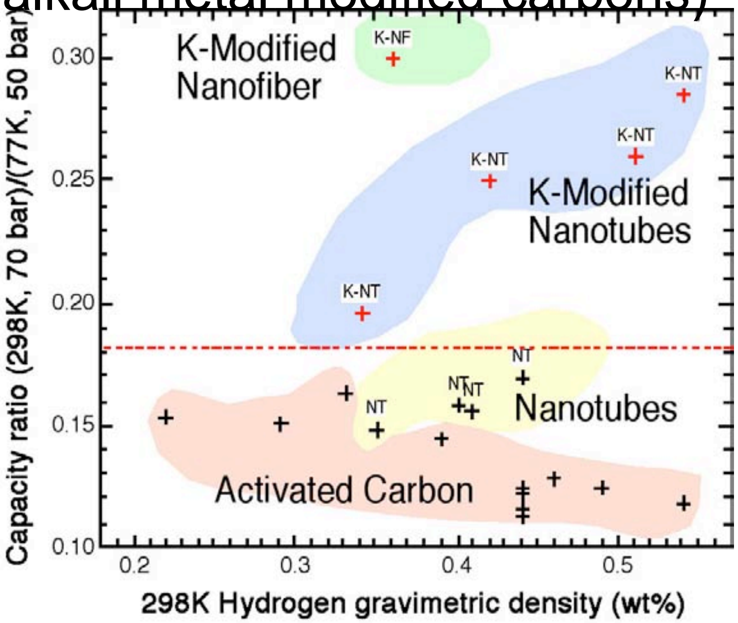
May 23-26, 2005

This presentation does not contain any proprietary or confidential information

Project ID # STP34 AHN

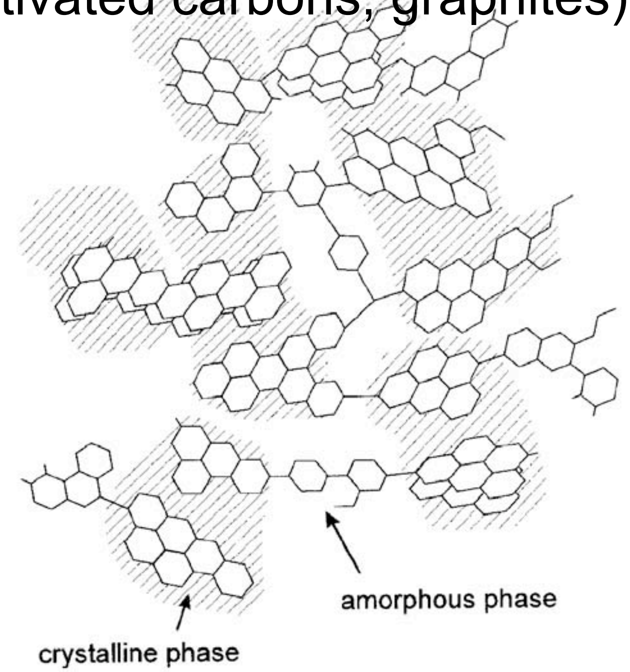
Approach

A. Local charge site polarization
(alkali metal modified carbons)



Ratio of hydrogen to carbon that can be accommodated in alkali-metal modified nanotubes. Note that in normal carbons, the ratio of hydrogen to carbon capacity of RT/77K is 1:6 while this ratio is 1:4 when the sorption potential is changed through K additions.

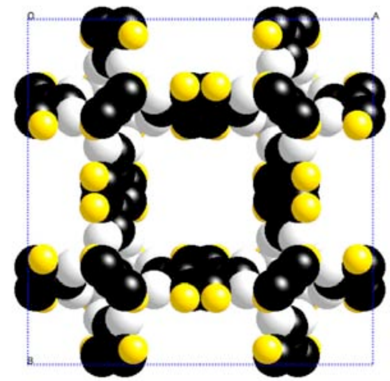
B. Polarization at heterogeneities
(activated carbons, graphites)



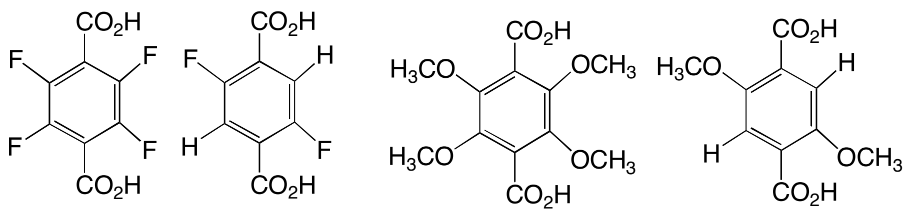
Engineer a high edge termination structure from graphite through mechanical attrition, and activate these edge sites with hydrogen or oxygen to promote high surface area hydrogen sorption.

Approach, cont'd

C. Modification of metal organic framework electron structures

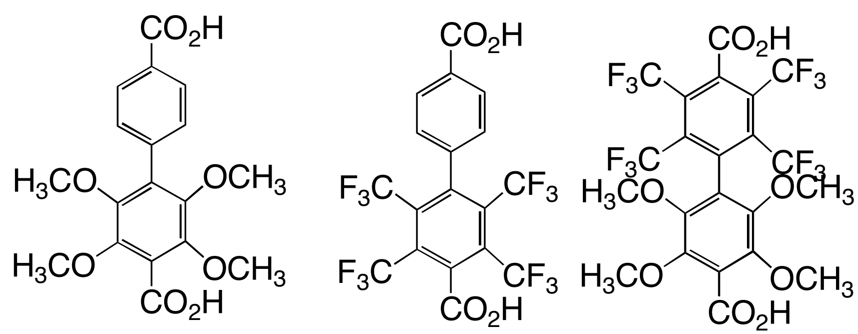


MOF-5 unit cell



A B C D

Above is a series of diacid structures that would be used in conjunction with MOF structure linkers in order to test the principle of enhanced edge site potentials for enhanced hydrogen sorption with symmetric polarization change.



Above are asymmetric polarization structures that will be used to verify hydrogen sorption properties

Examination of the Physical Aspects of Hydrogen Storage in MOFs

Omar M. Yaghi and Adam J. Matzger
Department of Chemistry
University of Michigan
Ann Arbor, MI 48109

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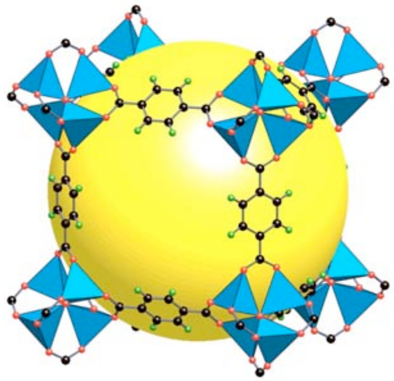
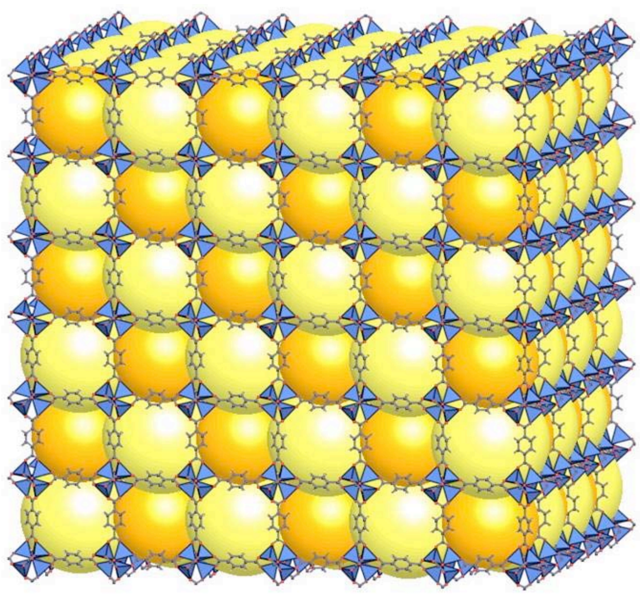
Project ID #
ST39 Yaghi

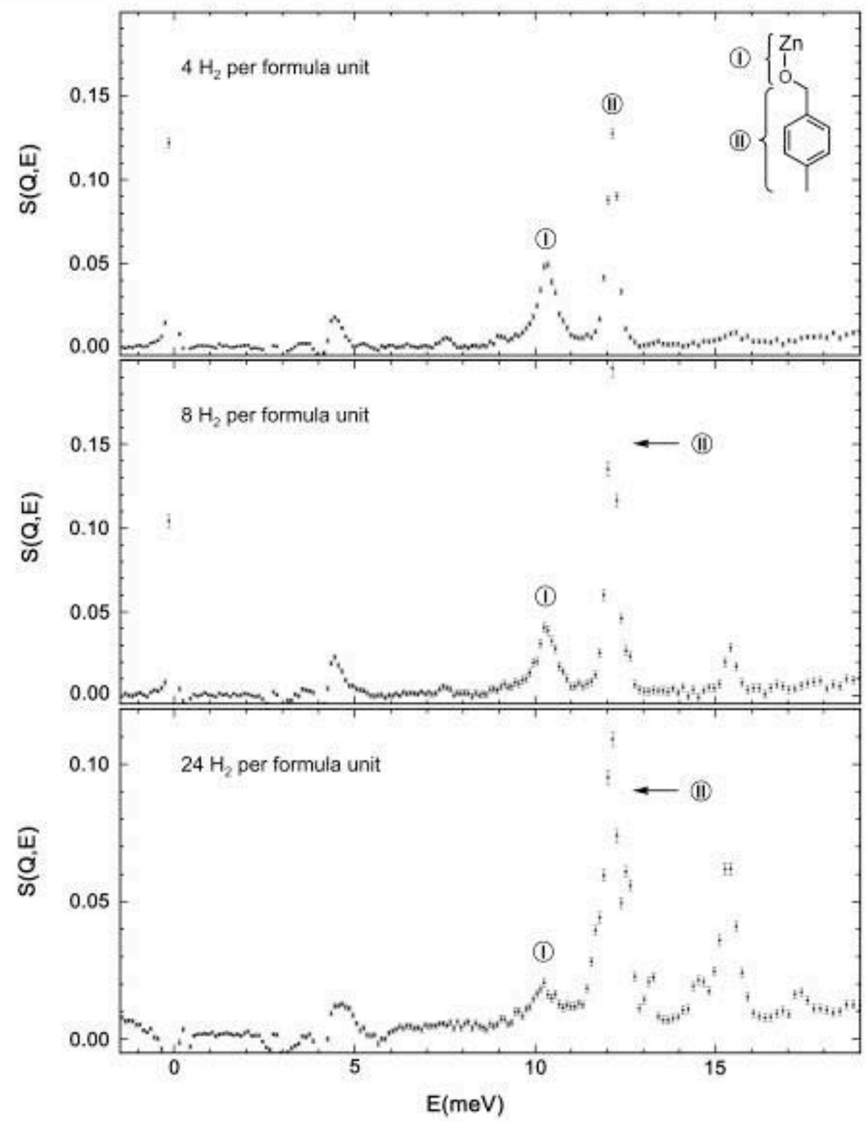
Inelastic Neutron Scattering of H_2 in MOF-5



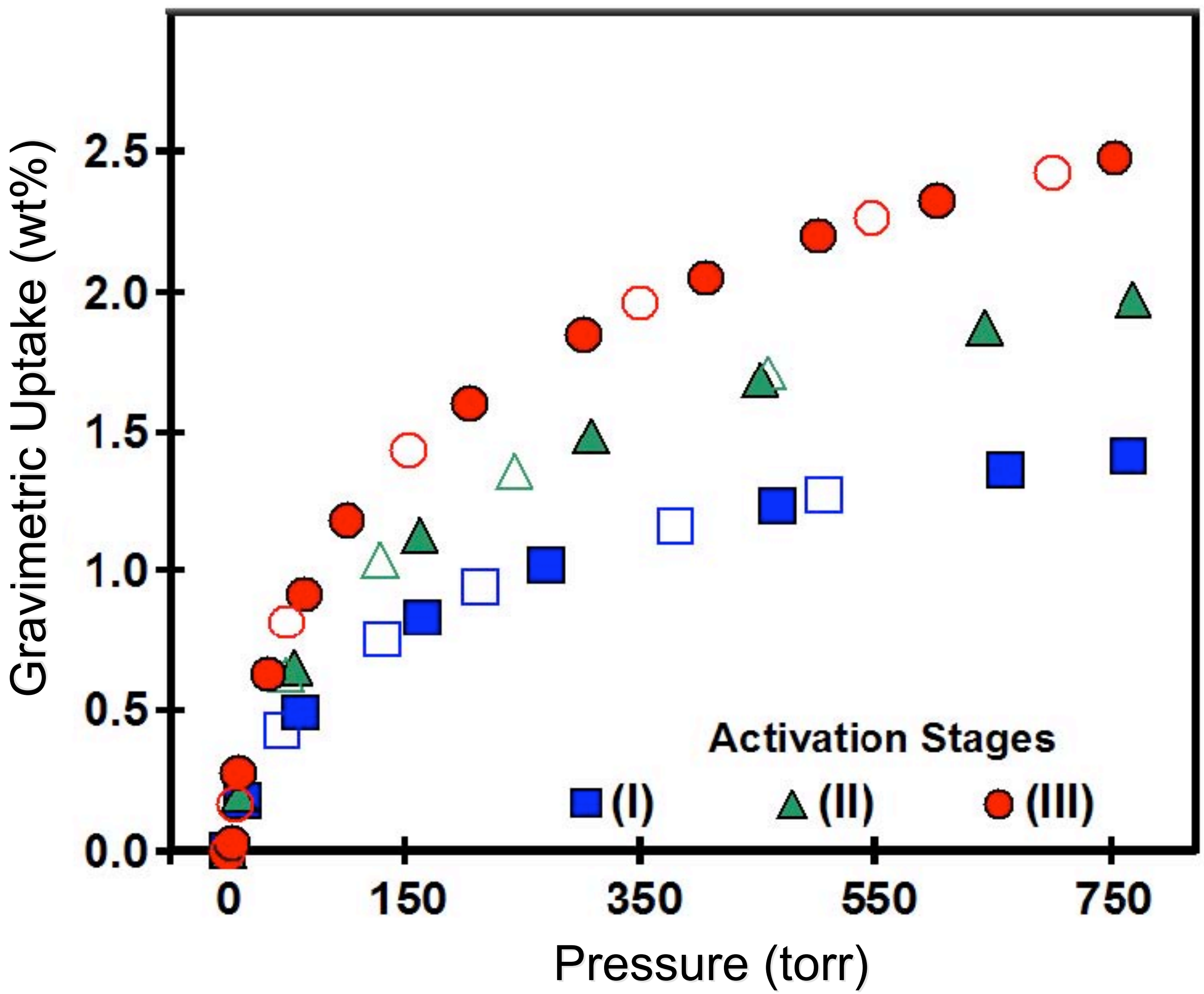
Smallest repeat unit of MOF-5

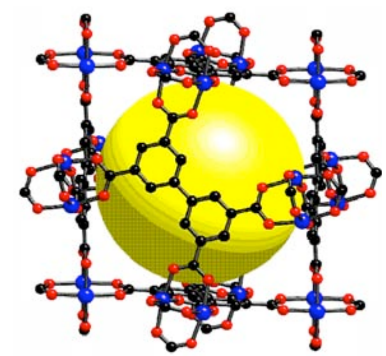


Extended structure of MOF-5



MOF-505 H_2 (77 K) Sorption Isotherms– Activation Study





MOF-505

Conducting Polymers as New Materials For Hydrogen Storage

Alan G. MacDiarmid
University of Pennsylvania

Part of the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

May 24, 2005

STP42

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KEY PARTS FROM CHO'S* PAPER

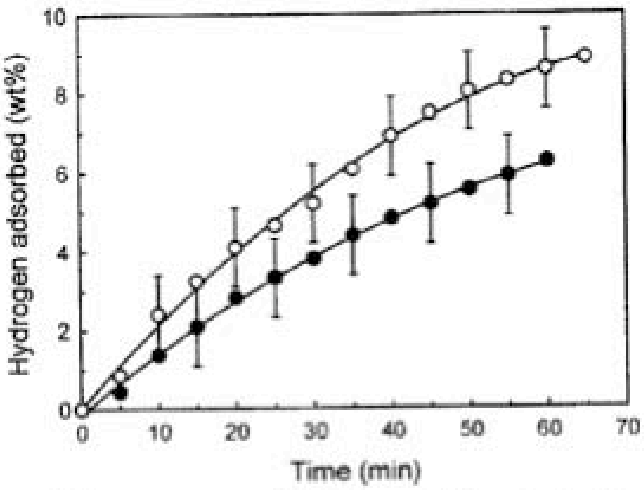


Figure 1. The amount of H_2 in wt. % for both (•) the PANI and (O) the Ppy treated with concentrated hydrochloric acid. The measurement was started after evacuation at 473 K and subsequently at room temperature at least 0.13 Pa.

Table 1. Summary of the hydrogen storage in metal hydrides, multiwalled carbon nanotubes and the acid treated conducting polymer measured using the same adsorption apparatus.

Sample	Press. (atm)/ Temp. (K)	Wt. %
† $MmNi_{4.7}Al_{0.3}$	10 ~ 20 / 298	1.2
† $MmNi_{4.8}Al_{0.2}$	10 ~ 20 / 298	1.3
$Ti_{0.7}Zr_{0.3}Mn_{1.0}Cr_{0.9}Ni_{0.02}Fe_{0.03}$	10 ~ 20 / 298	2.0
MWNT	90 / 298	0.8
HCl-Treated PANI	90 / 298	6.0
HCl-Treated Ppy	90 / 298	8.0

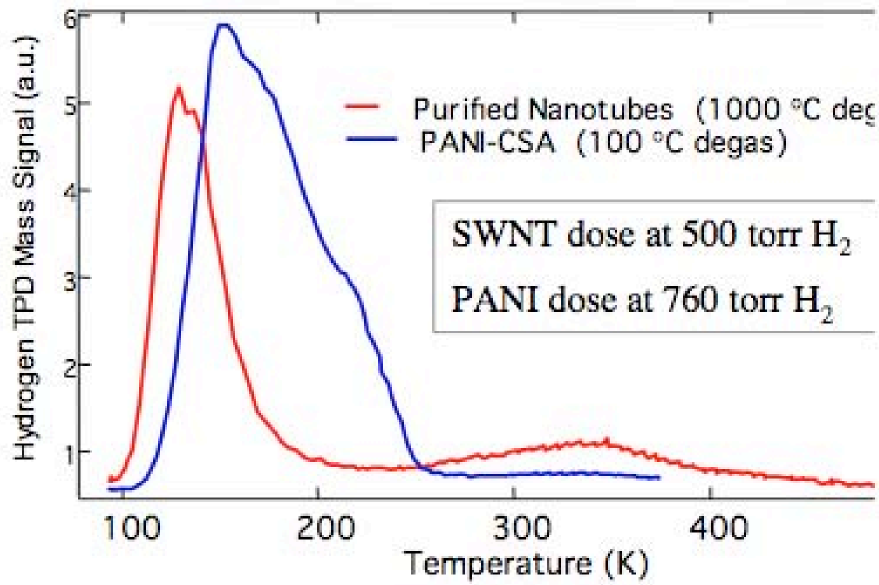
† = 'Mischmetals', i.e., a mixture of the early lanthanide metals, including

- Commercial (Aldrich) polyaniline (PANI) and polypyrrole used.
- The hydrogen storage can also be varied widely depending on the method of the modification process of the polymer using the concentrated hydrochloric acid, specifically, the exchange or removal level of the dopants, the drying temperature and the rigidity of the polymer backbone.

Results

Comparison of Conducting Polymers to SWNTs

- Very preliminary Temperature Programmed Desorption (TPD) studies by M. Heben Group at DOE labs, Golden, CO
- Polyaniline nanofibers doped with CSA (Camphorsulfonic Acid), PANI-CSA (one phase w/Triton X100 and stirring doped)
- Investigating the report By Cho et al.* of 6 wt% storage in PANI



- PANI-CSA: extremely broad desorption peak (~ -165 °C to -25 °C) with a shoulder at ~ -60 °C. This could indicate the presence of a variety of different binding sites and though it is not room temperature, it is quite accessible throu standard cooling methods.
- Potential roles of the surfactant and dopant are considered to be of very great importance for further study.

Synthesis and Processing of Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

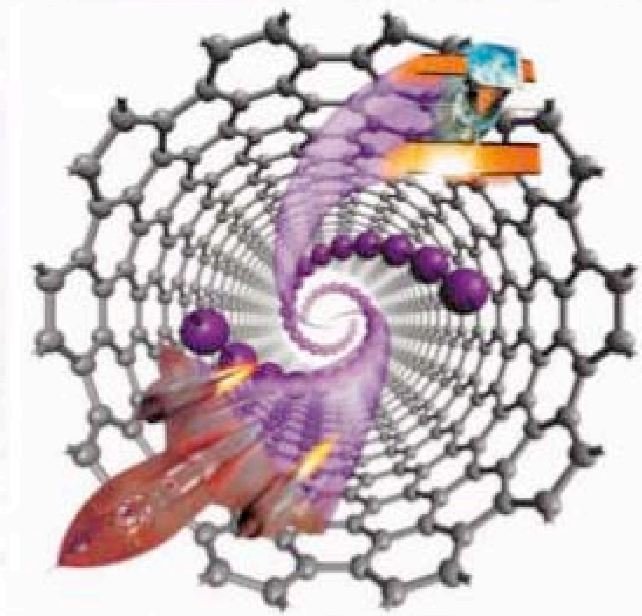
a participant in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials
DOE Hydrogen Program Annual Review, Washington, D.C., May 23, 2005

David B. Geohegan
Alex Puretzky*
Ilia Ivanov*
Hui Hu
Hongtao Cui
Christopher M. Rouleau
Zuqin Liu#

Condensed Matter Sciences Division
Oak Ridge National Laboratory

**Materials Science & Engineering Dept.,*
University of Tennessee

#Center for Nanophase Materials Sciences



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Project ID#
STP32

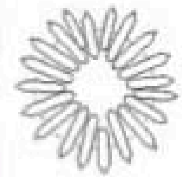
OAK RIDGE NATIONAL LABORATORY
U.S. DEPARTMENT OF ENERGY

P.O.C. David Geohegan, odg@ornl.gov

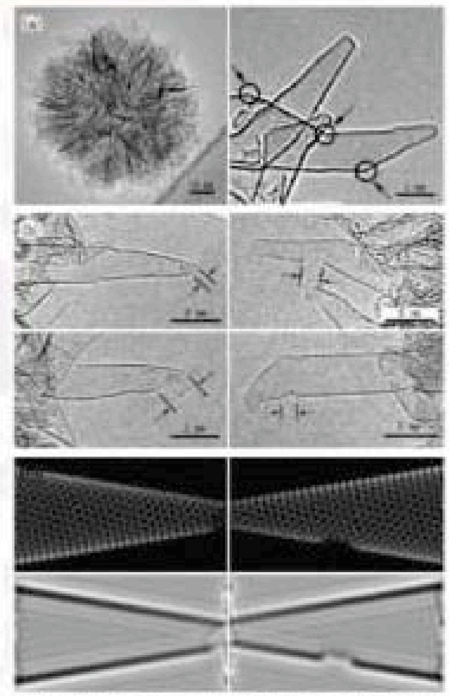
UT-BATTELLE

Why Single-Wall Carbon Nanohorns (SWNH)?

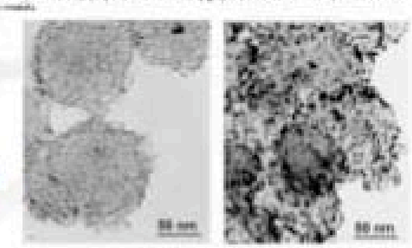
- **SWNH excellent as both storage vessels and catalyst supports**
  - **single-walled carbon structures like single-walled carbon nanotubes**
    - **huge surface area**
    - **visible in TEM**
    - **can be produced *without* metals**
    - **can be produced mixed with SWNT and metals to probe spillover mechanism**
  - **Two modes of storage**
    - **outer surface - initially exposed**
    - **inner surface accessible by opening pores**
    - **tiny "bottles" for storage**
  - **Excellent catalyst supports - for gas storage, fuel cells**
    - **nanohorn structure restricts catalyst aggregation, supporting finer catalysts at lower weight loadings**
    - **demonstrated by Iijima's group at NEC**
      - first commercial methanol fuel cell now in production for laptops



Schematic diagram of nanohorn aggregates. [Bekyarova'02]



TEM of SWNH as produced and after heat treatment [Aijima AM'04]



Pt nanoparticles on nanohorn aggregates (left) vs. carbon black (right). [Yoshitake PRB'04]

Study of Hydrogen Storage in Advanced Boron and Metal Loaded High Porosity Carbons Carried Out in the "DOE/NREL Center of Excellence on Carbon-based Hydrogen Storage Materials"

M. Chung, H.C. Foley, and P.C. Eklund

The Pennsylvania State University

5/23/2005

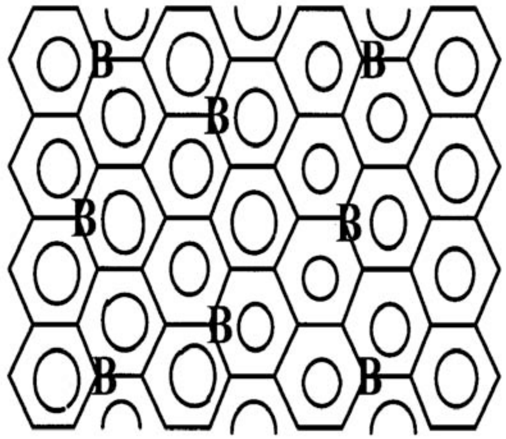
This presentation does not contain any proprietary or confidential information

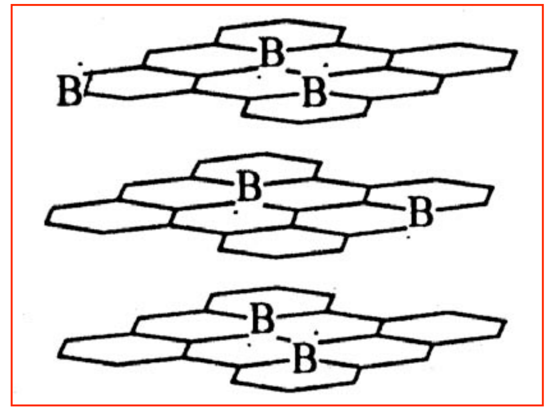
Project ID STP#36

Approach

- Synthesis of C-B-M Materials
  - Pyrolysis of Molecular Precursor *(Professor Mike Chung)*
  - Inclusion Reactions with Preformed High SSA Carbons *(Professor Henry Foley)*
  - Very High Temperature Gas Phase Synthesis *(Professor Peter Eklund)*
- Synthesis of highly micoporous C-B-M material by three separate routes.
- Characterization of the short- and long-range structure, the microporosity and SSA
- Evaluation of these materials for hydrogen sorption behavior.
- Optimization of the SSA for specific C-B-M materials of technological relevance

C/B Materials (B-substituted C)





- C and B with similar atomic size with trivalent coordination,
    - C/B material can maintain graphitic structure.
- B (electron deficiency) serves as p-type dopant
    - Increase π-electron delocalization and surface activities.

Metal-doped Carbon Aerogels for Hydrogen Storage

Joe H. Satcher, Jr., Theodore F. Baumann, Julie L. Herberg, Robert S. Maxwell

Lawrence Livermore National Laboratory

05/24/05

Project ID# STP-31

DOE Center of Excellence on Carbon-based H_2 Storage Materials

This presentation does not contain any proprietary or confidential information

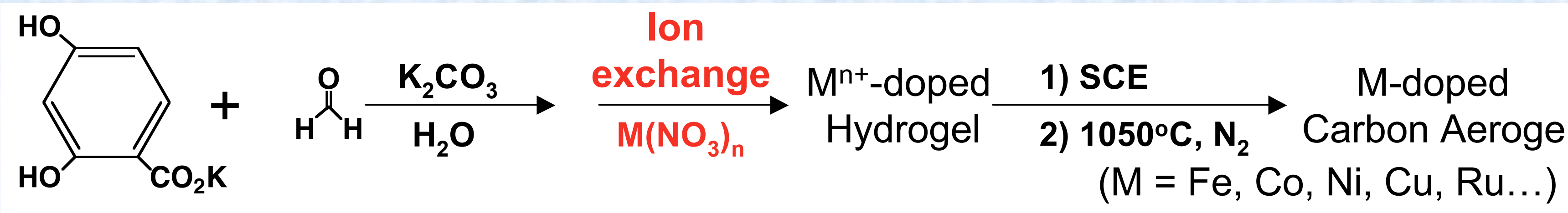
Work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48

Project Objectives

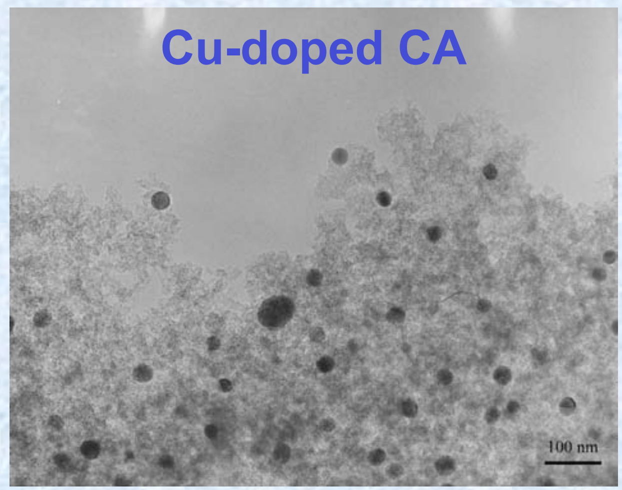
- To develop new nanostructured carbon materials that meet the targets set by DOE for hydrogen storage:
  - Novel metal-doped carbon aerogels (MDCAs) will be prepared, characterized and evaluated for their hydrogen storage properties
  - Mechanisms associated with hydrogen physisorption and chemisorption in these carbon-based materials will be investigated using advanced nuclear magnetic resonance (NMR) techniques
- Insights gained from MDCA systems should also be beneficial to the other nanostructured carbon systems, leading to the design of an optimized carbon-based material for hydrogen storage

Current Technical Status

- **Incorporation of metal species into aerogel framework using sol-gel precursors containing ion exchange sites :**
  - **General technique that can be used to incorporate a variety of metals**



- **Physical Properties:**
  - Density Ranges: 150-400 mg/cm^3
  - Surface Areas: 500-900 m^2/g
  - Metal Content: 1-10% by weight
- **Metal nanoparticles form during carbonization (5 to 60 nm)**



Satcher, J. H.; Baumann, T. F., *US Patent 6 613 809*, **2003**.

Baumann, T. F. et al *Langmuir*, **2002**, *18*, 7073; *Langmuir*, **2002**, *18,* 10100; *J. Non-Cryst. Solids* **2003**, *317*, 247 *J. Non-Cryst. Solids*, **2003**, *318, 223*.

Hydrogen Storage in Graphite Nanofibers and the Spillover Mechanism

A Study Carried Out in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

Anthony J. Lachawiec, Gongshin Qi and Ralph T. Yang (P. I.)

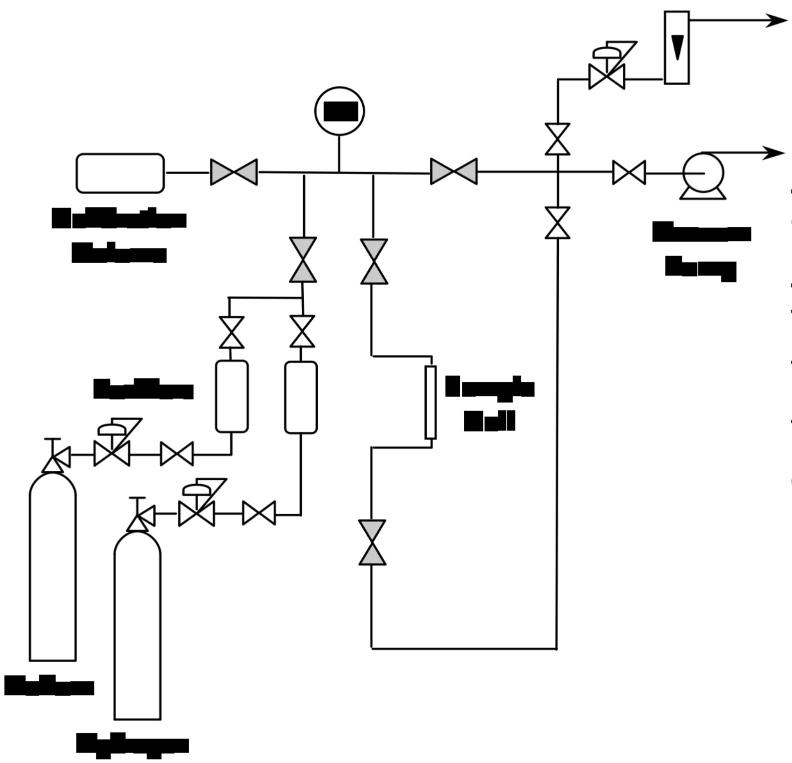
University of Michigan

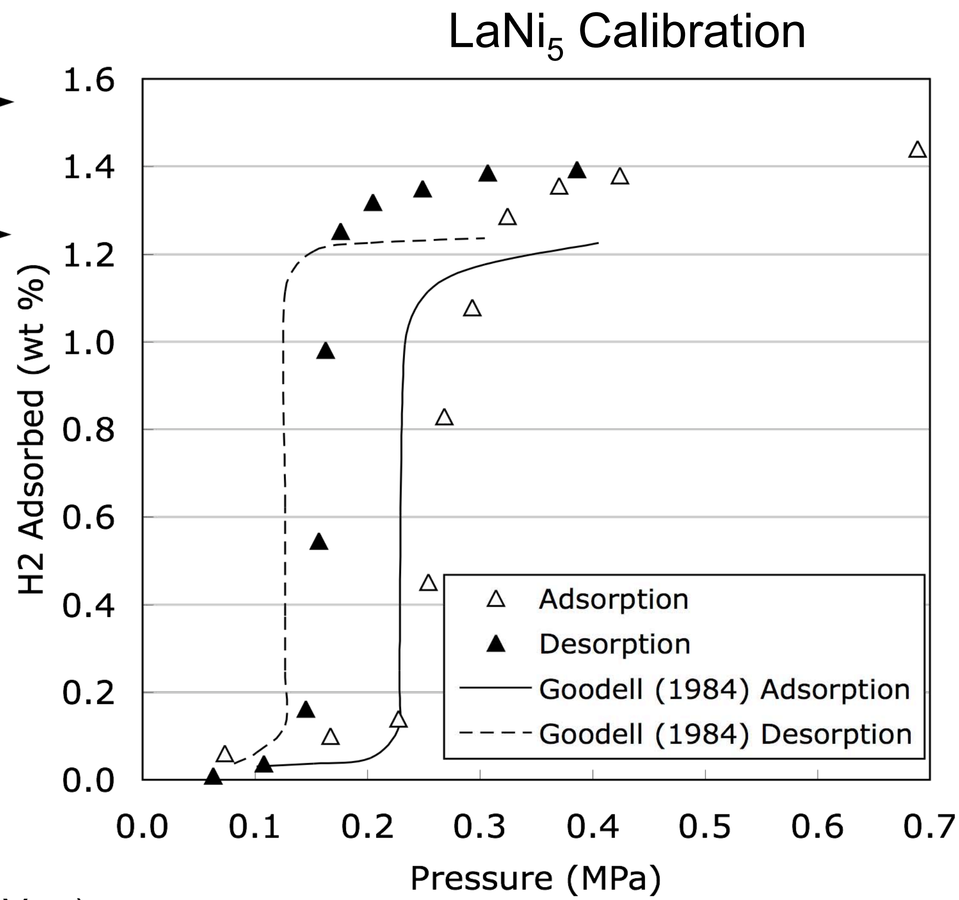
Department of Chemical Engineering

23-24 May 2005

STP40

High Pressure Measurement



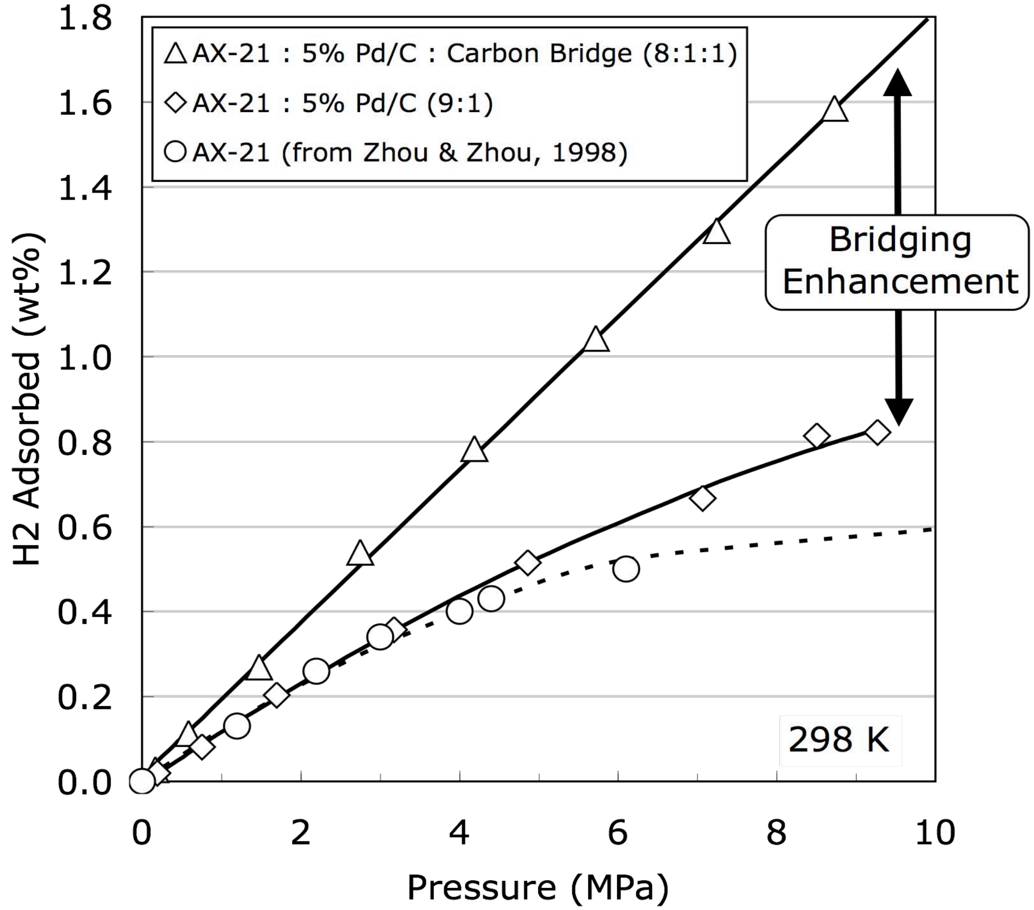


- Calibrated Volumetric System ($LaNi_5$ & $TiAl_{0.12}V_{0.04}$)
- In-situ Pretreatment to 1023 K (750 C)
- Adsorption Measurements to 12 MPa (1800 psia)

Source: Goodell (1984) *J. Less-Common Met.* 99, 1

High Pressure Spillover Enhancement

- Extension of low-pressure work
- Identical trends observed at high pressure
- Completely reversible adsorption at 298 K
- Adsorption capacity tripled at 10 MPa (only 1.3 times without bridges)
- 1.8 wt% capacity at 10 MPa without optimization



Sources: AX-21 Bridge Data: Unpublished Work, Lachawiec, Qi & Yang (2005)
AX-21 Isotherm: Zhou & Zhou (1998) *Chem Eng. Sci.* 53, 2531

University of Michigan
Department of Chemical Engineering

Characterization of Hydrogen Adsorption by NMR

"DOE Center of Excellence on Carbon-based Hydrogen Storage Materials"

Yue Wu
Department of Physics and Astronomy
And
Curriculum in Applied and Materials Sciences
University of North Carolina, Chapel Hill
May 23-26, 2005

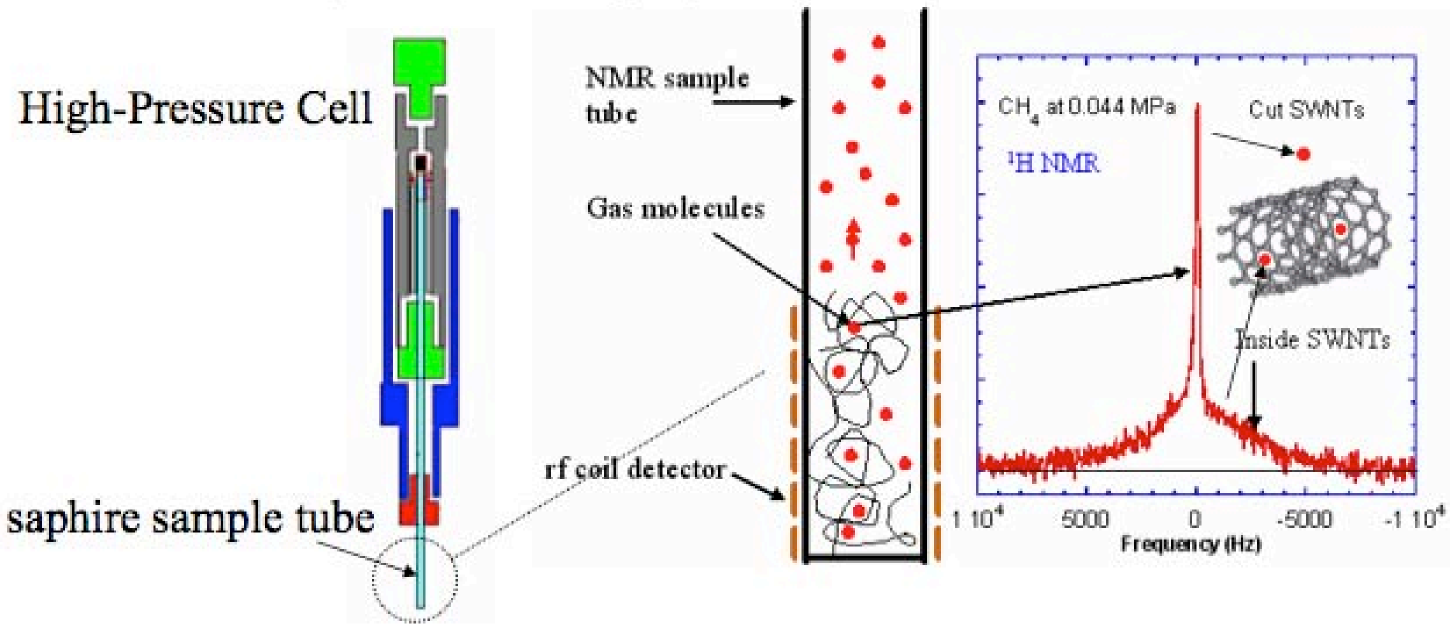
This presentation does not contain any proprietary or confidential information

Project ID #
STP41

Technical Accomplishments/ Progress/Results

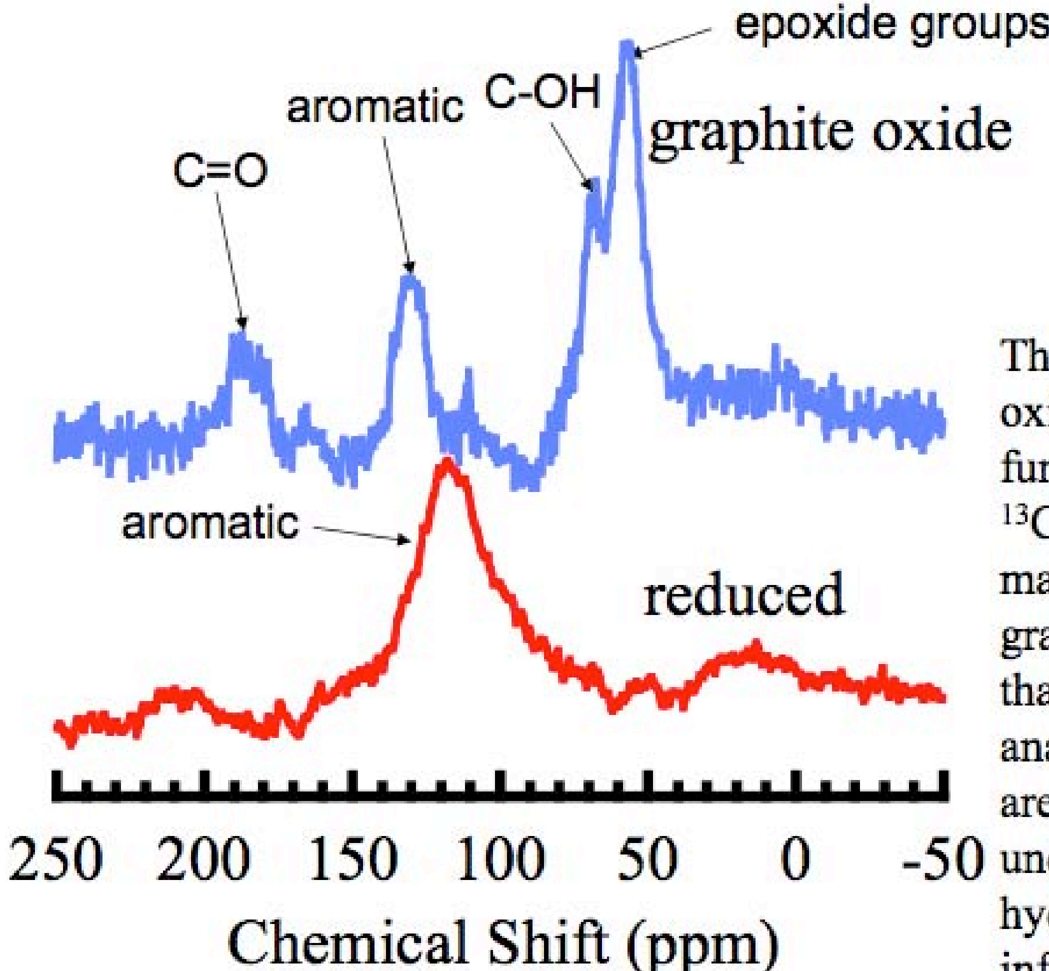
High-Pressure NMR Probe

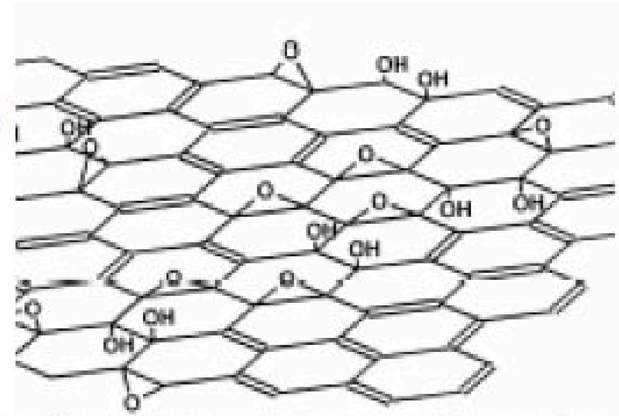
H_2 pressure ranging from 1-100 atmospheres is required for evaluating hydrogen adsorption in carbon-based materials. Therefore, we need to carry out NMR measurements under H_2 pressure up to 100 atm. A saphire-based high-pressure cell was built and tested successfully up to 100 atm. The high-pressure cell is incorporated in an NMR probe for high-pressure NMR measurements.



Proton NMR signal revealing both adsorbed (broad peak) and free gas (narrow peak) molecules in single-walled carbon nanotubes.

Technical Accomplishments/ Progress/Results





The ^{13}C NMR spectrum of graphite oxide reveals the details of the functional groups in this material. The ^{13}C NMR spectrum of the reduced material shows clearly the return to a graphitic structure. This demonstrates that ^{13}C NMR could be used to analyze the structure of high surface area carbon-based absorbents and understand the interactions with hydrogen. This could provide crucial information on hydrogen adsorption mechanisms.

Neutron Characterization of Carbon-Based Materials

carried out in the

DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

Craig Brown

Dan Neumann

NIST

National Institute of Standards and Technology

Technology Administration, U.S. Department of Commerce

(NCNR)

May 23th 2005

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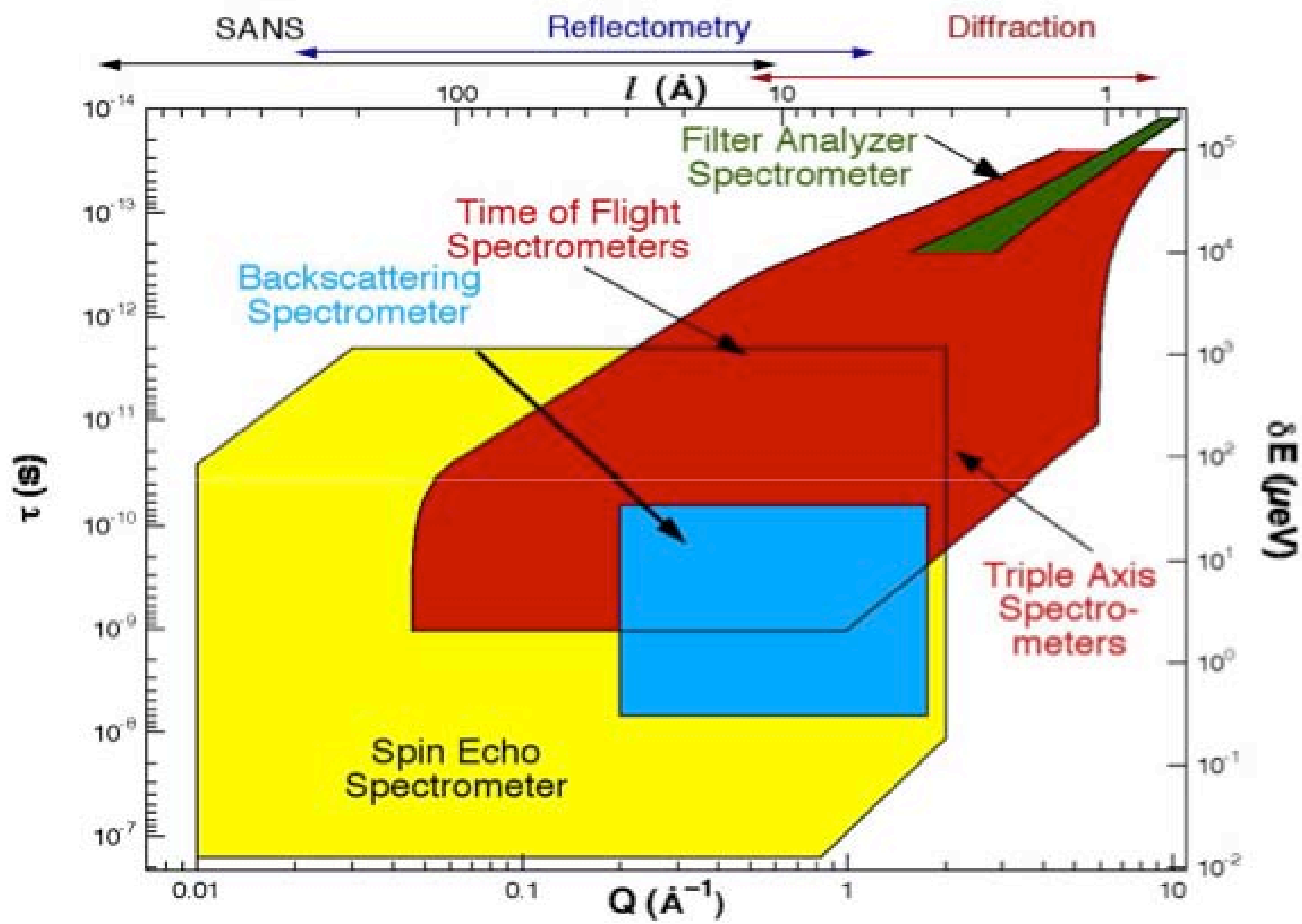
Approach

- neutron scattering will be used to address the following questions:
- **Where is the hydrogen?**
- **Is the hydrogen atomic or molecularly adsorbed?**
- **Can we identify adsorption sites and activation barriers?**
- **What are the diffusion mechanisms?**
- **How is the substrate influenced upon adsorption?**
- **Do sorption processes change as the system lengthscale decreases to the nanoscale?**
- **Does manipulating the host electronic structure change these processes?**

Approach


SANS
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Spectrometers
Backscattering
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τ (s)
δE (μeV)
Q (Å⁻¹)
0.01
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1
10

State of the Center of Excellence

- Detailed work statements for each partner with Go/No-Go decision points 24 months from start
- Project flow matches Grand Challenge time table
- All contracts are now in place
- Collaboration in earnest is beginning
- Center Safety plan reviewed by S. Weiner and colleagues - recommendations implemented
- Partner safety plansare being prepared
- Website and ftp site are operational
- Steering Committee has met and plans to meet regularly (Rice, Air Products and Chemicals, NREL)
- Center technical workshop this afternoon

Acknowledgments

- DOE HQ and GO Offices
- The Legal, Tech Transfer, and Contracts Offices at NREL and at all of the Partner Institutions
- Lynn Billman (NREL) - proposal management
- George Sverdrup / Satyen Deb / Sue Hock

- *And YOU - for your attention!*